QUARTERLY JOURNAL

OF THE

INDIAN CHEMICAL SOCIETY

VOLUME IV

1927

Journal of the Indian Chemical Society.

Vol. IV.   1927.

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CONTENTS—*continued.*

Vasicine—an Alkaloid Present in *Adhatoda Vasica*, Nees. Part II.

By Tarak Prasad Ghose.

In a previous communication (*J. Indian Chem. Soc.*, 1925, **1**, 315) it was shown that the leaves and tender twigs of *Adhatoda Vasica* contain an alkaloid, to which the name vasicine was given, and of which the empirical formula is $C_{11}H_{12}N_2O$. Although it contains two atoms of nitrogen, it is monobasic, giving only one series of salts. The nitrogen atom which shows basic properties gives a methiodide which, on being treated with barium hydroxide, gives a hydroxymethyl compound. Thus it behaves as a tertiary base.

Further work has been done to elucidate the constitution of this interesting alkaloid, and the present paper embodies the results so far achieved.

When vasicine is treated with phosphorus oxychloride and pentachloride it gives a crystalline chloro-compound. This substance is easily affected by light which turns it into a reddish brown resinous mass. Chlorovasicine is reduced to an oxygen-free base when it is treated with zinc and hydrochloric acid.

The main product of oxidation of vasicine with potassium permanganate is found to be 4-oxy-quinazoline (4-oxy- 1 : 3-benzdiazine). The melting point of this substance was observed to be 213·5-214°; its analysis, crystalline structure, and properties, such as sublimation, all agreed with those recorded for 4-oxy-quinazoline. According to Bogert and Gortner its melting point is 214° (*J. Amer. Chem. Soc.*, 1909, **31**, 123). For confirmation, 3-methyl-4-oxy-quinazoline was prepared from this substance. It melted at 71° when it contained one molecule of water of crystallization, and at 150° when it was anhydrous. The analysis also agreed with the formula. The recorded melting point of 3-methyl-4-oxy-quinazoline is 71° for the substance with one molecule of water of crystallization (Bogert and Geiger, *J. Amer. Chem. Soc.*, 1912, **34**, 526).

When vasicine is fused with potassium hydroxide, o-aminobenzoic acid and acetic acid are formed.

From the above experimental evidence it would appear that vasicine contains a 1:3-benzo-diazine nucleus and its structural formula would be (I). On oxidation with permanganate it yields 4-oxy-quinazoline (II).

(I).   (II).
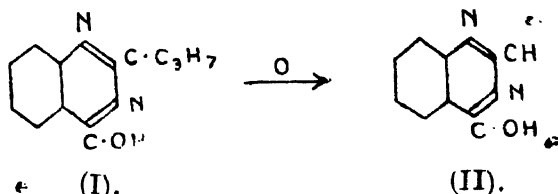
The mono-basic character of vasicine, its behaviour as a tertiary base and its yielding a chloro compound support the above view of its constitution. The fact that acetic acid is one of the products of alkali fusion of vasicine indicates that there is a CH_3 group present in the C_3H_7 group attached to the nucleus. Further experiments are in progress to elucidate the structure of this group.

It is of interest to note that, so far as the author is aware, this is the first time that a quinazoline base has been found to occur in nature.

<div align="center">EXPERIMENTAL.</div>

Chlorovasicine.—To cooled phosphorus oxychloride (50 g.) pure dry vasicine hydrochloride (9 g.) was added and the whole was kept cool. When complete solution was effected, phosphorus pentachloride (11 g.) was added. The mixture was kept cool for some time, afterwards it was allowed to attain room temperature (30°) and after two hours was heated on the water-bath for 30 minutes. The whole was then slowly poured into 750 c.c. of ice and water. The solution was filtered and neutralised with ammonia (a slight excess being used), keeping it cool while adding ammonia. After some time, fine flakes of chloro-vasicine crystallised out. These were collected and dried on porous plate and finally over sulphuric acid *in vacuo.* The dried crystals were dissolved in dry benzene and dry hexane added, when the chloro-compound was precipitated in fine crystalline flakes with a silvery lustre. These were dried *in vacuo* over sulphuric acid; m.p. 136-137°. Recrystallised once again, the melting point remained constant. This compound quickly decomposed and turned reddish brown when it was kept exposed to light. (Found: C, 63·6; H, 5·8; Cl, 17·1. $C_{11}H_{11}$ N_2Cl requires C, 63·9; H, 5·3; Cl, 17·0 per cent.).

Reduction Product of Chlorovasicine.—Chlorovasicine (5 g.) was reduced using hydrochloric acid (80 c. c.) and zinc dust (13 g.). Zinc was added in 3 instalments and the whole was finally heated on the water-bath for 15 minutes. It was allowed to cool when a double compound of zinc and the reduced base separated. This was dissolved in a small quantity of water and made alkaline with ammonia. Zinc was removed by passing hydrogen sulphide. The solution was rendered free from sulphuretted hydrogen by passing a current of air, and was then concentrated when crystals separated. The crystals were dissolved in chloroform and the alkaline mother-liquor was extracted with chloroform. On removing chloroform from the mixed solutions, some crystals separated. On recrystallization from hot water, they separated as prismatic needles. When allowed to dry on porous plate at room temperature the compound melted at 77°, and the substance contained two molecules of water of crystallization. When dried in a vacuum over sulphuric acid for several days it still retained half a molecule of water of crystallization and the melting point was 87-88°. Repeated recrystallization from dilute alcohol and subsequent drying as before, did not alter the melting point. The substance, m.p. 87-88°, was analysed. (Found: C, 72·7; H, 6·7; N, 15·7. $C_{11}H_{12}N_2,\frac{1}{2}H_2O$ requires C, 72·9; H, 7·1; N, 15·5 per cent.).

Hydrochloride of the reduced Base.—The base was suspended in alcohol and concentrated hydrochloric acid was added till all the base had dissolved. The solution was filtered and warmed and then ether was added slowly till there was a slight opalescence. On standing, the hydrochloride separated as fine prismatic needles. Dried in a vacuum over sulphuric acid, the substance melted at 255-256°. Recrystallization did not alter the melting point. (Found: Cl, 16·2. $C_{11}H_{12}N_2$, HCl requires Cl, 16·8 per cent.)

Chloroplatinate of the reduced Base.—The chloroplatinate, prepared in the usual way, was an orange yellow substance. (Found: Pt, 25·4. $C_{11}H_{14}N_2,PtCl_6$ requires Pt, 25·9 per cent.).

Oxidation of Vasicine.—Vasicine (20 g.) was dissolved in dilute sulphuric acid, making the solution faintly acid. The solution was made up to 500 c.c. and oxidized at a temperature of 15-20° by dropping in potassium permanganate solution (5 per cent.) and keeping the mixture stirred mechanically. About 2 litres of permanganate solution were required to complete the reaction. The precipitated manganese dioxide was removed and repeatedly washed with boiling

water till the washings were colourless. The filtrate and washings were evaporated on the water-bath, a slow current of CO_2 being passed into it all the while. When it was concentrated to a small bulk it was acidified with dilute H_2SO_4 and steam distilled. No volatile acid could be obtained. After steam distillation, the liquid was neutralized with sodium carbonate and evaporated to dryness. The dry salts were extracted with hot alcohol (95 per cent.). The alcohol was then distilled off. The salts obtained were again dissolved in water and precipitated with silver nitrate. A curdy gelatinous precipitate was obtained. This was washed till free from silver nitrate, suspended in water, warmed and decomposed with sulphuretted hydrogen. The precipitated silver sulphide was removed by filtration and hydrogen sulphide was removed from the filtrate by drawing a current of air through it. On cooling a crop of yellowish brown crystals separated. These were removed and on concentration, the mother-liquor yielded a further crop of crystals.

These crystals were sparingly soluble in cold water but readily dissolved in hot water. They were easily soluble in alcohol but sparingly so in ether. On recrystallization from hot water, they came out in fine silky needles slightly yellow in colour, m.p. 212°. On recrystallizing once again they came out in slightly yellow silky needles, m.p. 213·5—214°. The substance was sublimed. The sublimate was recrystallized from water when it came out in fine white silky needles, m.p. 213·5—214°. (Found: C, 66·1; H, 4·3; N, 19·1. $C_8H_6N_2O$ requires C, 65·8; H, 4·1; N, 19·2 per cent.).

This substance when treated with chloro-platinic acid, gave an orange yellow precipitate, which was recrystallised from hot dilute alcohol. The salt was dried at 110° and analysed. (Found: Pt, 27·5. $C_8H_6N_2OPtCl_6$ requires Pt, 27·9 per cent.). This substance is 4-oxy-quinazoline.

3-Methyl-4-oxyquinazoline.—This substance was prepared from 4-oxy-quinazoline by direct methylation with methyl iodide and potassium hydroxide in methyl alcohol solution as suggested by Bogert and Geiger (*loc. cit.*). The substance which came out in fine crystalline needles was recrystallized twice from hot water, m.p. 71°. Bogert and Geiger give the melting point as 71° for the substance with one molecule of water of crystallization. The substance was recrystallized from dry chloroform and dried in a vacuum over sulphuric acid for several days. The anhydrous substance melted at 104-105° which is the recorded melting point of the anhydrous

substance (*loc. cit.*). (Found: N, 17·8. $C_9H_8N_2O$ requires N, 17·5 per cent.).

Fusion of Vasicine with Potassium Hydroxide.—Vasicine (5 g.) was gradually added to a melt of potassium hydroxide (20 g.) and water (20 c.c.) heated to 150° on an oil-bath. The temperature of the bath was raised and the mixture kept thoroughly stirred. At 190° the whole became a viscous horny mass. The mixture melted between 200 and 210° to a thin liquid. Above 220° it began to froth. The temperature of the bath was raised to 250°. After cooling, the fused mass was dissolved in water (100 c.c.). It was allowed to cool and shaken up with ether to remove a basic substance, the quantity of which was too small for examination. The alkaline solution after extraction with ether was acidified with sulphuric acid and steam-distilled. The distillate was collected in three fractions.

The silver salt of the first fraction was prepared and analysed. (Found: Ag, 64.3. CH_3COOAg requires Ag, ·64·6 per cent.).

The other fractions of the distillate contained very little acid, and sufficient silver salt for analysis could not be prepared.

After steam distillation the solution was neutralized with sodium carbonate and evaporated to dryness. The dry salts were extracted with alcohol. Alcohol was distilled off and the salts were dissolved in water and precipitated with silver nitrate. The silver salts were washed and decomposed with sulphuretted hydrogen. Silver sulphide was removed and the solution was rendered free from sulphuretted hydrogen by a current of air. The solution showed a distinct blue fluorescence. The free acids were extracted with ether and recrystallized from water, m.p. 144-145°. The substance was sublimed. The sublimate separated from water as long flattened needles which were dried in a vacuum over sulphuric acid, m.p. 145°. (Found: C, 61·5; H, 5·4·C,H_7NO requires C, 61·3; H, 5·1 per cent.).

The silver salt of the acid was prepared and analysed. (Found: Ag, 44·1. $C_7H_6NO_2Ag$ requires Ag, 44·26 per cent.).

This acid is therefore *o*-amino-benzoic acid. For confirmation the melting point of a mixture of this acid with *o*-amino-benzoic acid from another source was determined; m.p. 145°.

Researches in the Thiazole Series. Part I. Action of Hydrochloric Acid on Allylthiosemicarbazide.

By Satish Chandra De.

By the action of bromoalkylamines on potassium thiocyanate Gabriel (*Ber.*, 1889, **22**, 1139, 2230, 2984) obtained substances which he called derivatives of ψ-propylene thiocarbamide and which are now known to be derivatives of thiazole. Also Prager (*Ber.*, 1889, **22**, 2991), on condensing allylamine with mustard oils, obtained products, which, on treatment with hydrochloric acid, were transformed into thiazole derivatives.

The above results led me to try the action of hydrochloric acid on various 4-allylthiosemicarbazides. It should be mentioned that Busch and Lotz (*J. pr. Chem.*, 1914, **90**, 270) tried the action of boiling hydrochloric acid on 4-allylthiosemicarbazide; they found that the semicarbazide either remained unchanged or decomposed into its components on prolonged boiling.

The author has obtained from 4-allylthiosemicarbazide a hydroxylmethylthiazole (II) which appears to be formed by the decomposition of the hydrazine derivative (I) first formed.

(I).   (II).
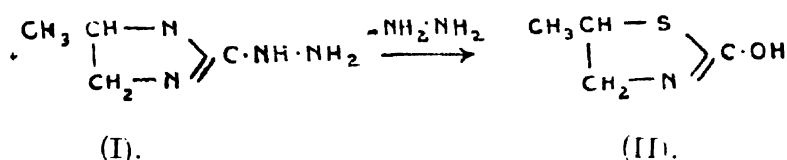
It was then thought that by substituting acetyl, benzoyl, or phenyl in the hydrazine residue of allylthiosemicarbazide, a thiazole derivative might be obtained that on hydrolysis would give a thiazole hydrazine. But during acetylation of allylthio-semicarbazide an acetyl derivative of allylimino-*C*-methylthiobiazole was formed (Pulvermacher, *Ber.*, 1894, **27**, 626). The benzoyl derivative could be prepared and when treated with hydrochloric acid it was transformed not into a thiazole but into a thiobiazole derivative, the reaction proceeding according to the scheme—
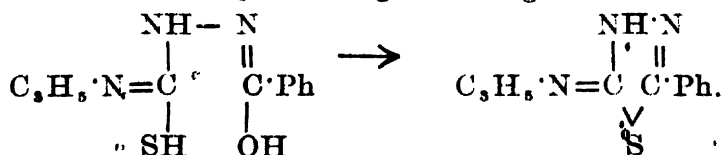
Substitution by phenyl group, as in 1-phenyl-4-allylthiosemi-carbazide, led to the formation of a thiazole derivative.

A further attempt was made to prepare a thiazole hydrazine by means of benzylideneallylthiosemicarbazide; this led to hydroxymethylthiazole. When the hydrazine residue in allylthiosemicarbazide was substituted by the phenyl thiocarbimide group the resulting allylanilidothiosemicarbazide yielded a thiobiazole derivative. The process possibly took place according to the scheme—

$$C_3H_5 \cdot N = \overset{\displaystyle NH \cdot NH}{\underset{\displaystyle SH}{\overset{|}{C}}} \quad \overset{\displaystyle}{\underset{\displaystyle NHPh}{\overset{|}{CS}}} \quad \xrightarrow{\quad -PhNH_2 \quad} \quad C_3H_5 \cdot N = \overset{\displaystyle NH \cdot NH}{\underset{\displaystyle S}{\overset{|}{C}}} \quad \overset{\displaystyle}{\underset{\displaystyle V}{\overset{|}{CS}}}$$
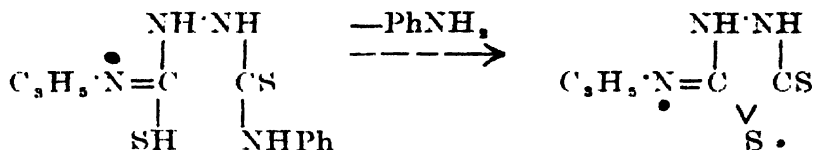
From these experimental facts it appears that if the 1-position in allylthiosemicarbazide is unsubstituted the thiazole hydrazine probably first formed readily parts with the hydrazine residue and hydroxymethylthiazole results; but if this position is occupied by certain groups or radicals then either a thiazole or a thiobiazole ring is formed. The question which groups or radicals favour the formation of one ring or the other is now under investigation and will form the subject of a subsequent communication.

EXPERIMENTAL.

Hydroxymethylthiazole.—4-Allylthiosemicarbazide (10 g.) was heated with concentrated hydrochloric acid (20—25 c.c.) in a sealed tube at 100° for 2—3 hours. After cooling the tube contained a small quantity of crystals of hydrazine hydrochloride which were separated ; when the filtrate was diluted with water and then saturated with ammonia, the free base separated in needles or rectangles having a faint reddish tinge. Crystallised from boiling benzene it formed white needles, m.p. 200°. The yield was very poor. The substance is easily soluble in alcohol and benzene but insoluble in water. (Found: S, 27·12. C_4H_7ONS requires S, 27·35 per cent.)

Acetylmethylthiazole.—The monoacetyl derivative was prepared in the usual way by heating for 10—15 minutes. On cooling crystals separated which were collected and crystallised from alcohol in needles, m.p. 242°. (Found: S, 20·28. $C_6H_9O_2NS$ requires S, 20·13 per cent.).

Benzoylmethylthiazole.—The hydroxymethylthiazolone was warmed with benzoyl chloride for a few minutes and the excess of benzoyl chloride was destroyed by means of alkali. The benzoyl

derivative so obtained formed a semi-solid mass which was allowed to remain in the alkaline solution for about two days when it gradually solidified. The solid mass was collected, finely powdered and triturated with an alkaline solution and filtered. The residue was washed with water and crystallised from alcohol, m.p. 243°. (Found : S, 14·66. $C_{11}H_{11}O_2NS$ requires S, 14·48 per cent.).

Nitrosomethylthiazole.—An aqueous solution of sodium nitrite was added to the hydrochloric acid solution of hydroxymethyl-thiazole cooled in ice. The nitroso-derivative separated at once in the form of a yellow precipitate which was filtered, washed with water and crystallised from acetic acid : light yellow needles, m.p. 138°. (Found : S, 21·67. $C_4H_6O_2N_2S$ requires S, 21·92 per cent.).

Phenylhydrazidomethylthiazole.—Molecular quantities of allyl mustard oil and phenylhydrazine were mixed together in a flask. The reaction began with evolution of heat and after a few minutes the whole mass assumed a jelly-like appearance. The reaction was brought to completion by heating on a water-bath for half an hour. The product was dissolved in boiling alcohol and from this solution 4-allyl-1-phenylthiosemicarbazide separated in long white needles, m.p. 119°. This semicarbazide (10 g.) was heated with concentrated hydrochloric acid (20 c.c.) in a sealed tube at 100° for 2 hours. After cooling, the tube contained crystals having a light tinge and the acid solution had a pink colour. These crystals were collected and dissolved in water, boiled with animal charcoal, and the filtrate concentrated when the hydrochloride of phenyl-hydrazidomethylthiazole separated in colourless needles, m.p. 203°. To obtain the free base the following method was found best : the aqueous solution of the hydrochloride was warmed on a water-bath and to the hot solution ammonia was slowly added until neutral, when the base separated in almost white plates. These were collected, washed and dried. So obtained the substance melted at 92° and was used for the preparation of its derivatives. For analysis a portion was dissolved in alcohol, the solution boiled with animal charcoal and from the filtrate it was precipitated by water in white plates, m.p. 94°. (Found : S, 15·68. $C_{10}H_{11}N_3S$ requires S, 15·46 per cent.).

The *acetyl derivative* was prepared in the usual way. It was purified from alcohol when it was obtained as white needles, m.p. 190°. (Found : S, 13·16. $C_{12}H_{13}ON_3S$ requires S, 12·85 per cent.)

The *benzoyl derivative* prepared in the ordinary way, solidified on long standing. The solid was collected and crystallised from boiling benzene. It is insoluble in alcohol, ether, chloroform and cold benzene and moderately soluble in hot benzene. (Found: S, 10·38. $C_{17}H_{17}ON_3S$ requires S, 10·29 per cent.)

The *benzylideneallylthiosemicarbazide* was obtained by adding the equivalent quantity of benzaldehyde to a hot alcoholic solution of 4-allylthiosemicarbazide. After a few minutes white needles of the benzylidene compound separated which was crystallised from rectified spirit in needles, m.p. 125°. (Found: S, 14·49. $C_{11}H_{13}N_3S$ requires S, 14·38 per cent).

Benzylidenehydrazidomethylthiazole.—The benzylidene compound (15 g.) was heated with concentrated hydrochloric acid (30 c.c.) in a sealed tube at 100° for two hours. The contents of the tube were diluted with water and saturated with ammonia when the free base separated in white rectangular crystals. It was purified from alcohol from which it crystallised in shining rectangles, m. p. 141°. (Found: S, 14·69. $C_{11}H_{13}N_3S$ requires S, 14·38 per cent.). On hydrolysis it gave the hydroxymethylthiazole previously described.

The *acetyl derivative* was prepared and crystallised from alcohol in white needles, m.p. 119°. (Found: S, 12·42. $C_{13}H_{15}ON_3S$ requires S, 12·26 per cent).

The *benzoyl derivative* separated from alcohol in white rectangles, m. p. 150°. (Found: S, 10·22. $C_{18}H_{17}ON_3S$ requires S, 9·91 per cent.).

The *nitroso derivative* was obtained by adding an aqueous solution of sodium nitrite to the cold hydrochloric acid solution of the thiazole. The yellow precipitate was filtered, washed with water and crystallised from alcohol in yellow needles, m.p. 120° with decomposition. (Found: S, 12·68. $C_{11}H_{12}ON_4S$ requires S, 12·90 per cent.)

Acetylallylimino-C-methylthiobiazole.—Allylthiosemicarbazide was boiled with acetic anhydride. The acetyl derivative separated on cooling and crystallised from alcohol in needles, m.p. 79°. When the acetyl compound was deacetylated with hydrochloric acid it gave the hydrochloride of allylimino-*C*-methylthiobiazole (m.p. 173°) which on neutralisation with ammonia yielded the base as a crystalline mass. It crystallised from alcohol in white plates and melted at 126° and was identical with Pulvermacher's compound obtained from allylthiosemicarbazide and acetyl chloride.

Allylimino-C-phenylthiobiazole.—4-Allyl-1-benzoylthiosemicarbazide was prepared from allylthiosemicarbazide and benzoyl chloride in chloroform solution ; the product crystallised from boiling water in needles, m. p. 172°. On heating this benzoyl compound with hydrochloric acid in a sealed tube at 100° it was converted into the hydrochloride of the above thiazole (m.p. 112°). The free base was obtained by saturating the dilute acid solution with ammonia. Crystallised from dilute alcohol it melted at 118°. It was identical with the compound obtained from 4-allyl-1-benzoylthiosemicarbazide and acetyl chloride (*Ber.*, 1894, **27**, 628).

Allyliminothiobiazolethiol.—Allylthiosemicarbazide was converted into allylthiocarbanilidothiosemicarbazide by boiling with phenyl mustard oil in alcoholic solution for two minutes. The solid product was filtered and washed with alcohol. It was thus obtained in plates, m.p. 183°. This thiosemicarbazide was then heated in a sealed tube at 100° with concentrated hydrochloric acid for two hours. On cooling a white precipitate separated. The mother-liquor, on dilution with water, became turbid and after some time deposited a further quantity of the white substance. For purification it was dissolved in dilute sodium hydroxide solution and precipitated by dilute acid. Crystallised from boiling water in plates it melted at 136°. (Found: N, 24·37. $C_8H_7N_3S_2$ requires N, 24·28 per cent.). From the dilute acid solution on neutralisation with alkali a small quantity of another substance was obtained which could not be purified and studied.

Oxidation of Benzylidenemethyl-thiazole hydrazine and Hydroxymethylthiazole.—The hydrochloride of each (8 g.) was shaken up with excess of bromine water and the mixture was first warmed on a water-bath and finally heated to boiling over a free flame. The mixture was then evaporated to dryness when a brown syrup was left behind. This was extracted with alcohol and the alcoholic solution allowed to stand for a long time in a desiccator. The crystals that separated were collected and crystallised from water. It was found to be identical with the ψ-methyltaurin of Gabriel and Prager (*loc. cit.*).

Interaction of Sulphuryl Chloride with Substances Containing the Reactive Methylene (CH₂) Group.

Interaction of Sulphuryl Chloride with Substances Containing the Reactive Methylene (CH$_2$) Group.

By Kuverji Gosai Naik and Mohanlal Laxmidas Shah.

The reactivity of the hydrogens of a methylene ($-CH_2-$) group in compounds containing $-CO \cdot CH_2 \cdot CO-$ and $-CN \cdot CH_2 \cdot CO-$ has been taken advantage of in numerous condensations. Some light has been thrown on the factors which govern the reactivity of the methylene group, in substituted malonamides, with the help of sulphur monochloride (Naik, *J. Chem. Soc.*, 1921, **119**, 379 ; 1921, **119**, 1231 ; Naik and Avasare, *ibid*, 1922, **121**, 2592; Naik and Patel, *J. Indian Chem. Soc.*, 1924, **1**, 27). It was decided to carry this subject further by studying the interaction of substituted malonamides and sulphuryl chloride. The results show that sulphuryl chloride can react as a chlorinating agent on the methylene group, and, also, in certain cases, on aromatic nuclei. [1]

In view of chlorination having been already effected with the help of sulphuryl chloride, it was expected that in the substituted malonamides containing aromatic nuclei, the chlorine might attack both the methylene group and the aromatic nucleus, and that only when the reactivity of both the hydrogens of the methylene group $-CH_2-$, was sufficiently modified by the proximity of other groups, that sulphuryl chloride would attack the nucleus. This has been found to happen in certain cases.

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[1] Chlorination with sulphuryl chloride seems to have been studied by various workers (*Zeit. Chem. von Beilstein u. Hubner*, 1866, **2**, 705; Dubois, *Bull. Acad. roy. Belg.*, 1876, **42**, 126; Töhl and Elurhardt, *Ber.*, 1893, **26**, 2940; Peratoner, *Gazzetta*, 1894, **24**, 1, 236; Wöhl, D.R.-PP. 139552, 1467/1902, 160102/1902, 162394/1903; Silberrad, *J. Chem. Soc.*, 1921, **119**, 2029; *ibid*, 1922, **121**, 1015; Durrans, *J. Chem. Soc.*, 1922, **121**, 44; Elber and Klemm, *Ber.*, 1922, **55**, 217; Macbeth, *J. Chem. Soc.*, 1922, **121**, 1116; *ibid*, 1923, **123**, 1122; Durrans, *J. Chem. Soc.*, 1923, **123**, 1424; Bulow and King, *Annalen*, 1924, **439**, 211; Fuchs and Katscher, *Ber.*, 1924, **57**[B], 1256; Silberrad and Parke. *J. Chem. Soc.*, 1925, **127**, 1724; Silberrad, *J. Chem. Soc.*, 1925, **127**, 2677.)

The main results of the interaction of sulphuryl chloride with various mono- and di-substituted amides of malonic and methylmalonic acids can be summarised as under :—

      Conversion of the group $-CH_2-$ *into* CCl_2,

      (*a*) without chlorination of the nucleus: malondiphenyl-amide, malondibenzylamide, malondi-*o*-tolylamide, malon-di-*p*-tolylamide; malon-dipropylamide and malon-mono-*p*-tolylamide undergo this change ;

      (*b*) with chlorination of the nucleus; malon-di-*m*-tolylamide, malon-mono-phenylamide and malon-di-*β*-naphthylamide undergo this change.

II.   *Conversion of the group* $-CH_2-into-CHCl-$

      (*a*) without chlorination of the nucleus: malon-di-methylphenylamide undergoes this change ;

      (*b*) with chlorination of the nucleus: malon-di-*o* naphthylamide undergoes this change.

III. *Conversion of the group* $-CH(CH_3)-$ *into* $CCl(CH_2Cl)$: methylmalondiphenylamide, methylmalon-di-*o*-tolylamide and methylmalon-di-*p*-tolylamide undergo this change.

    Type I. (*a*). Malondiphenylamide reacts with sulphuryl chloride as under :—

$$(PhNH.CO)_2CH_2 + 2Cl_2SO_2 = (PhNH.CO)_2CCl_2 + 2HCl + 2SO_2.$$
$$\tag{1}$$
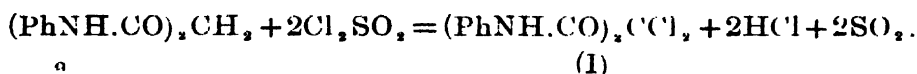
That the substance produced from malon diphenylamide has the constitution follows from the facts enumerated below :—

(1) The two hydrogen atoms that are replaced by chlorine, are not supplied by the phenyl group because (*a*) a similar dichloro-derivative is obtained from malondipropylamide; (*b*) the chlorine atoms can be replaced again by hydrogen with production of the original amide by the action of sodium hydrosulphide (Brand, *Ber.*, 1906, **42**, 3464), and by potassium iodide and hydrochloric acid (Meyer, *Annalen*, 1911, **380**, 212).

(2) The hydrogen atoms that are replaced by chlorine are not attached to the nitrogen atoms, because malon-dimethylanilide, where there is no hydrogen attached to the nitrogen, yields a mono-chloro-derivative.

    Type I (*b*).. In the case of malon-*m*-tolylamide, the reaction was more vigorous (giving rise to a tetrachloro-derivative) than with the corresponding *o*- and *p*-compounds.

$$(C_7H_7.NH.CO)_2CH_2 + 4SO_2Cl_2 = (C_7H_6Cl.NH.CO)_2CCl_2$$
$$+ 4HCl + 4SO_2$$
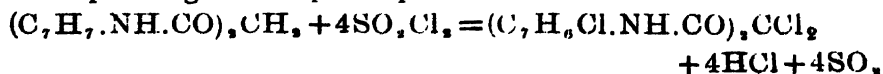
Of the four chlorine atoms present in this compound, two are attached to the methylene carbon as is evident by the reduction with potassium iodide and concentrated hydrochloric acid. The other two halogen atoms which are present in the compound, even after reduction, may be present either in the ortho- or para-position to the amino-group in the aromatic nucleus.

On studying the behaviour of malon-di-β-naphthylamide with sulphuryl chloride, there was a copious evolution of hydrogen chloride and sulphur dioxide. The tetrachloro-compound thus formed lost, on reduction by the above method, two atoms of chlorine, which were attached to the methylene carbon. Malon-monophenylamide exhibits a similar reactivity, and the reaction proceeds as under :—

$$\begin{array}{l} NH_2 \cdot CO \\ > CH_2 + 3SO_2Cl_2 = \\ C_6H_5 \cdot NH \cdot CO \end{array} \quad \begin{array}{l} NH \cdot CO \\ > CCl_2 + \ SO_2 + 3HCl \\ C_6H_4Cl \cdot NH \cdot CO \end{array}$$
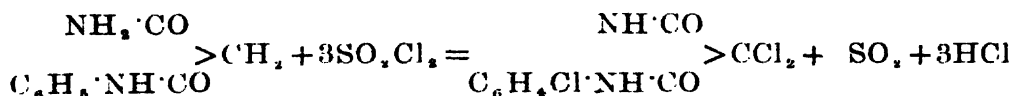
Type II (a). The interaction of malon-dimethylphenylamide with sulphuryl chloride results in the production of a mono-chloro compound.

$$[CH_3(C_6H_5) \ N \cdot CO]_2 CH_2 + SO_2Cl_2 = [CH_3(C_6H_5)N \cdot CO]_2 CHCl + HCl + SO_2.$$
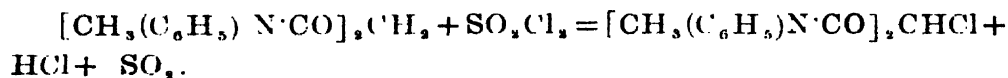
In spite of the two hydrogen atoms of the methylene group being available only one is attacked. This course of the reaction is not an abnormal one, as is evident from the work of Naik (loc. cit.) and West (J. Chem. Soc., 1922, **121**. 2196).

Type II (b). When α-naphthylamide was made to react with sulphuryl chloride in the ratio of 1 : 3, a trichloro-compound was obtained.

$$(C_{10}H_7 \cdot NH \cdot CO)_2 CH_2 + 3Cl_2SO_2 = (C_{10}H_6Cl \cdot NH \cdot CO)_2 CHCl + 3HCl + 3SO_2$$
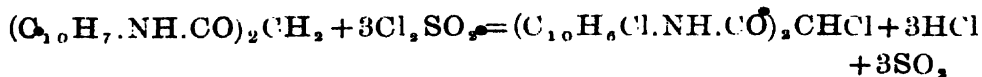
That in this trichloro-compound, only one chlorine is attached to the methylene carbon, and the other two are substituted in the aromatic nuclei, is shown by the study of its reduction with potassium iodide and hydrochloric acid.

It is curious that malon-di-α-naphthylamide gives a trichloro-derivative, whereas the corresponding β-compound gives a tetrachloro-derivative under similar conditions. That the difference between the behaviour of α-naphthyl compounds and β-naphthyl

compounds is general was noticed by other workers (Whiteley, *J. Chem. Soc.*, 1903, **83**, 24), and was attributed to various reasons (Weinberg, *Ber.*, 1924, **54[B]**, 2168).

Type III. Further, it was desirable to see if the same type and reactivity persisted amongst the corresponding derivatives of methylmalonic acid. Here one of the hydrogen atoms of the methylene group is replaced by the methyl group, so that a monochloro derivative might be expected on interaction with sulphuryl chloride. Yet, in the three cases that were studied, dichloro-derivatives were formed. On reduction of these by the usual method it was found that both the chlorine atoms were replaced by hydrogen. Hence the second chlorine atom must have entered the methyl radicle. If the second chlorine atom had entered the benzene nucleus, it could not have been reduced by the above method, nor could it have come in place of the hydrogen of the imino $(-NHR-)$ group, as was pointed out previously. Thus :

$$(R \cdot NH \cdot CO)_2 CH \cdot CH_3 + 2SO_2Cl_2 = (R \cdot NH \cdot CO) \, CCl \cdot CH_2Cl + 2HCl + 2SO_2$$
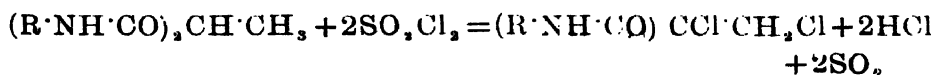
(where R represents either a phenyl or a tolyl group).

The above dichloro-compounds showed no trace of any free hydrogen chloride contained in them; for, when they were shaken with water, the filtrate gave no reaction with silver nitrate. Examples of chlorination similar to this are known (*cf.* Willgerodt and Durr, *Ber.*, 1887, **20**, 539). The mechanism of this interesting course of chlorination is discussed later on.

Coming to the question of reactivity of the hydrogens of the methylene group in grouping such as $-CO \cdot CH_2 \cdot CO-$, $-CN \cdot CH_2 \cdot CO-$ etc., it is interesting to note that the experiments described here afford clear evidence that the interaction of sulphuryl chloride with compounds containing the methylene radicle depends on the total negativity of the groups attached to the two remaining valencies of the carbon atom (*loc. cit.*) If these valencies carry neutral groups such as $\cdot CO \cdot NH_2$, as in malonamide no interaction occurs with sulphuryl chloride. If, however, the neutral character of either or both of the carboxylamide groups is disturbed by the entrance of phenyl, tolyl, etc., interaction with sulphuryl chloride readily occurs.

The reactivity of sulphuryl chloride with malonic ester, aceto-acetic ester, cyanacetic ester, etc., has been studied by Macbeth (*J. Chem. Soc.*, 1922, **121**, 1120 ; 1923, **123**, 1125), who obtained

chloro-compounds. In all such cases, the reactivity of the sulphuryl chloride with esters was found to be great, certainly greater than the reactivity of the corresponding amido and substituted amido derivatives.

Although no definite measurements have as yet been made, it is evident that the speed of the reaction depends on the total negativity of the attached groups. For example, sulphuryl chloride reacts more vigorously with compound (*iii*, R = Ph) than with (*ii*, R = Tol) whilst the reaction with the ester itself is the most vigorous, even taking place at the ordinary temperature. So in a series like

    (*i*) $CH_2 \cdot (CONH_2)_2$

    (*ii*) $NH_2 \cdot CO \cdot CH_2 \cdot CO \cdot NHR$ (R = Ph, Tol etc.)

    (*iii*) $CH_2 \cdot (CONHR)_2$

    (*iv*) $CH_2 \cdot (COOC_2H_5)_2$

the reactivity which is absent in (*i*) is found in (*ii*) and goes on increasing through the series (Naik, *loc. cit.*).

The reactivity of the CH_2 group may be referred to (*a*) polarity (Macbeth and his collaborators, *J. Chem. Soc.*, 1922, **121**, 892, 904, 1109, 1116, 2169, 2527, 2601 ; 1923, **123**, 124, 1122 ; 1925, **127**, 892, 1118), (*b*) to keto-enol transformation (Thorpe and his collaborators, *J. Chem. Soc.*, 1911, **99**, 2183; 1921, **119**, 1203; 1922, **121**, 1896), or (*c*) to the combined influences of polarity effects, steric influence and structural characteristics such as would give rise to keto-enol transformations (West, *J. Chem. Soc.*, 1924, **125**, 710).

The reactivity of the compounds investigated herein can be explained on the basis of keto-enol transformation. In the cases where both the hydrogens of the methylene group are replaced by chlorine atoms, the substance, according to Norris and Thorpe (*J. Chem. Soc.*, 1921, **119**, 1203), assumes an enolic form. Thus in the case of formation of compound 1, the course followed can be represented thus :

$$PhNH \cdot CO \cdot CH_2 \cdot CO \cdot NHPh \longrightarrow PhNH \cdot CO \cdot CH \cdot CH : C(OH) \cdot NHPh$$
$$\overset{Cl_2}{\longrightarrow} PhNH \cdot CO \cdot CH : C(OC)' \cdot NHPh$$
$$\text{unstable}$$
$$\longrightarrow PhNH \cdot CO \cdot CHCl \cdot CO \cdot NHPh.$$
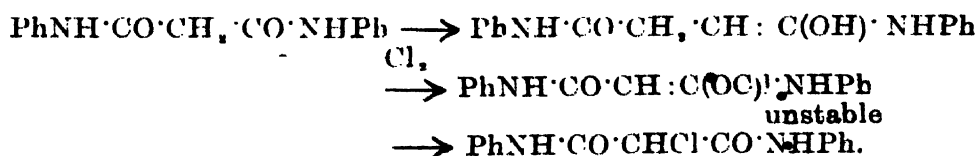
By a similar series of changes the final product is the dichloro-compound, $CCl_2(CONHPh)_2$.

In the case of malon-dimethylphenylamide, only one hydrogen is reactive. It appears that after one of the two Hydrogen atoms has reacted, the other becomes sluggish, only a monochloro-compound being obtained. West (*loc. cit.*) has shown that further chlorination of this amide is not possible on passing more chlorine. This sluggishness of the second hydrogen atom can be explained as being due to the stability of the keto-form as in the case of acetyl acetone (Norris and Thorpe, *loc. cit.*), which gives a monobromo-compound, $(CH_3 \cdot CO)_2 CHBr$. Further bromination does not take place.

In some cases, however, enolisation involves a hydrogen atom of a terminal methyl group. For example, in the case of methylma-londiphenyl amide, after the group $-C(CH_3)Cl$ has been formed, enolisation involves a hydrogen atom of the methyl group:

$$
\begin{array}{ccc}
CH_3 & & CH_2 \quad OH \\
| & & | \quad >C< \\
Cl \cdot C{-}CO \cdot NHPh & \longrightarrow & Cl \cdot C \qquad NHPh \\
| & & | \\
CO \cdot NHPh & & CO \cdot NHPh \\
& & \text{enolic form}
\end{array}
$$

$$
\begin{array}{ccc}
CH_2 \quad OCl & & CH_2Cl \\
| \quad >C< & & | \\
Cl{-}C \qquad NHPh & & Cl{-}C{-}CO \cdot NHPh \\
| & \longrightarrow & | \\
CO \cdot NHPh & & CO \cdot NHPh \\
\text{unstable} & &
\end{array}
$$
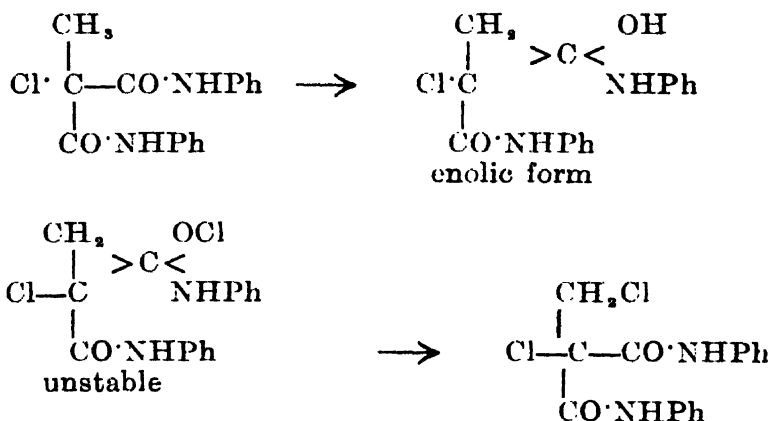
Such a change due to the enolisation of a terminal methyl group was noticed by Hantzsch (*Ber.*, 1894, **27**, 356, 3168).

EXPERIMENTAL.

Dichloromalondiphenylamide.

Malondiphenylamide (2 g.) was made to react with sulphuryl chloride (2·25 g.) in presence of dry benzene (50 c.c.). The mixture was refluxed for four hours over a water-bath. Dense fumes of sulphur dioxide and hydrogen chloride were evolved. When the reaction was over, the solution was filtered hot and the filtrate, on cooling, deposited a white crystalline mass. This was filtered, washed repeatedly with dry petroleum to free it from excess of sulphuryl chloride, and crystallised from hot benzene, m.p. 127°.

It is fairly soluble in acetone, chloroform, ethyl acetate and nitrobenzene, sparingly so in benzene, alcohol, toluene, acetic acid and carbon tetrachloride, and insoluble in light petroleum. (Found: Cl, 21·8. $C_{13}H_{11}N_2O_2Cl_2$ requires Cl, 21·96 per cent.).

Reduction of the above Compound with Hydriodic Acid.—The dichloro-compound (0·1498 g.) was dissolved in absolute alcohol (30 c.c.). To the solution, potassium iodide (1·85 g.) dissolved in water (20 c.c.) was added, and then concentrated hydrochloric acid (10 c.c.). The mixture was refluxed for 3 hours at about 60°. A control experiment was set up at the same time with the same amount of absolute alcohol, potassium iodide and concentrated hydrochloric acid, for the same period; and from the observations in the control experiment, a correction was introduced in the observations of the actual reduction experiment. The substance liberated iodine equivalent to 19·3 c.c. of 0·0971N sodium thiosulphate solution. (Found: Cl (equivalent of the iodine liberated), 22·16. $C_{13}H_{11}N_2O_2$ Cl_2 requires Cl, 21·96 per cent.).

Reduction of Dichloromalondiphenylamide with alkaline Hydrosulphide.—The chloride (2 g.) was added to absolute alcohol (20 c.c.) and refluxed for about half an hour. An aqueous solution of sodium hydrosulphide, prepared by saturating sodium hydroxide (0·3 g.) dissolved in a small quantity of water with hydrogen sulphide, was gradually added to it. After a time the whole went into solution with a brown colour. On cooling a slight crystalline precipitate appeared. The solution was diluted with water (500 c.c.) and filtered. The substance was washed free from alkali by hot water. The product was then crystallised from acetic acid, and was found to be pure malondiphenylamide, m.p. 224-225°.

Dichloromalon-dibenzylamide.

This substance was prepared from malon-dibenzylamide (2 g.), and sulphuryl chloride (2 g.) in presence of dry benzene (50 c.c.) as before. It was deposited as a white mass sparingly soluble in benzene, from which it was crystallised in white shining plates, m.p. 170-171°.

It is fairly soluble in chloroform, sparingly so in benzene, alcohol, acetone, toluene, acetic acid, carbon tetrachloride, ethyl acetate, carbon bisulphide, ether and nitrobenzene, but insoluble in light petroleum. (Found: Cl, 19·82. $C_{17}H_{16}O_2N_2Cl_2$ requires Cl, 20·20 per cent.).

3

Dichloromalon-di-o-tolylamide.

This substance was prepared from malon-di-o-tolylamide (2 g.) and sulphuryl chloride (2 g.) in the usual way. The white solid is sparingly soluble in alcohol, from which it was crystallised in white needles, m.p. 140-141°.

It is fairly soluble in acetone, chloroform, ethyl acetate, carbon bisulphide and nitrobenzene, sparingly so in benzene, alcohol, toluene, acetic acid, carbon tetrachloride and ether, but insoluble in light petroleum. (Found: Cl, 20·15. $C_{17}H_{16}O_2N_2Cl_2$ requires Cl, 20·20 per cent.).

Dichloromalon-di-p-tolylamide.

The above compound was obtained as a white amorphous powder when malon-di-p-tolylamide (2 g.) was treated with sulphuryl chloride (2 g.) in the usual way. It was crystallised from alcohol in shining white needles, m.p. 145-146°.

It is fairly soluble in benzene, acetone, cloroform, toluene, acetic acid, ethyl acetate, carbon bisulphide, ether and nitrobenzene, sparingly so in alcohol and carbon tetrachloride, but insoluble in light petroleum. (Found: Cl, 20·01. $C_{17}H_{16}O_2N_2Cl_2$ requires Cl, 20·20 per cent.).

Dichloromalon-dipropylamide.

It was prepared by the action of sulphuryl chloride (3 g.) on malon-dipropylamide (2 g.) in the usual way. The solid product was crystallised from benzene in shining cubes, m.p. 108-109°.

It is fairly soluble in acetone, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, ethyl acetate carbon bisulphide, ether and nitrobenzene, but insoluble in light petroleum. (Found: Cl, 27·83. $C_9H_{16}O_2N_2Cl_2$ requires Cl, 27·82 per cent.).

Dichloromalon-mono-p-tolylamide.

It was prepared from malon-mono-p-tolylamide (2 g.) and sulphuryl chloride (2 g.) in the usual way. A white solid was obtained, which on crystallisation from benzene melted at 145-146°.

It is fairly soluble in acetone, ethyl acetate and ether, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon bisulphide and nitrobenzene, but almost insoluble in petroleum and carbon tetrachloride. (Found· Cl. 27·1. $C_{10}H_{10}O_2N_2Cl_2$ requires Cl, 27·17 per cent.).

Preparation of Malon-di-m-tolylamide.

Malonic ester and pure m-toluidine were taken in molecular proportions in a flask provided with a cork, through which a wide tube passed. This tube was bent at the top and was fitted into a condenser. The length of the tube from the cork upwards to the bend at the top measured 15 cm. The flask was put in a paraffin-bath and maintained at 130-149° for four hours, when alcohol distilled off drop by drop. The temperature at the end was raised to 150°. The rate of the distillation was so regulated that for every drop of alcohol distilled, fifteen drops of the liquid returned to the flask. This increased the yield of the diamide. The liquid was then transferred to a mortar, where it solidified on cooling. The solid was extracted with alcohol and finally washed with a little ether. When crystallised from acetic acid, it was obtained in brilliant needles, m.p. 152°.

It is fairly soluble in chloroform, ethyl acetate and nitrobenzene, sparingly so in benzene, alcohol, acetone, toluene, acetic acid, carbon tetrachloride, carbon bisulphide and ether, but almost insoluble in light petroleum. (Found : N, 9·8. $C_{17}H_{14}O_2N_2$ requires N, 9·9 per cent.).

Dichloromalon-di-m-tolylamide dichloride.

On treating malon-di-m-tolylamide (2 g.) with sulphuryl chloride (4 g.) in the usual way a white mass was deposited on standing. The resulting product was crystallised from benzene in cubic crystals, m.p. 164°.

It is fairly soluble in acetone, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, ethyl acetate, ether and nitrobenzene, but almost insoluble in carbon tetrachloride and light petroleum. (Found : Cl, 33·51. $C_{17}H_{14}O_2N_2Cl_4$ requires Cl, 33·78 per cent.)

Dichloromalon-monochlorphenylamide.

This compound was prepared from malon-mono-phenylamide (2 g.) and sulphuryl chloride (3 g.) in the same way as the preceding chloride. After the reaction was over, the product crystallised immediately on cooling. On recrystallising from benzene, it yielded shining pearly plates, m.p. 136°.

It is fairly soluble in acetone, ethyl acetate and ether, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, carbon bisulphide and nitrobenzene, but almost insoluble in light petroleum. (Found : Cl, 37·67. $Cl_6H_7O_2N_2Cl_2$ requires Cl, 37·80 per cent.)

Dichloromalon-di-β-naphthylamide dichloride.

The above compound was obtained as a white amorphous powder, when malon-di-β-naphthylamide and sulphuryl chloride were treated in the usual way. It was crystallised from benzene, in which it is difficultly soluble, in shining crystals, m p. 183°.

It is sparingly soluble in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, ethyl acetate and nitrobenzene, but almost insoluble in light petroleum, acetone, carbon bisulphide and ether. (Found : Cl, 29·25. $C_{23}H_{14}O_2N_2Cl_4$ requires Cl, 28·84 per cent.)

Monochloromalon-dimethylphenylamide.

Malondimethyl-phenylamide (2 g.) and sulphuryl chloride (2 g.) were made to react in the usual way described. The amorphous white product, when crystallised from absolute alcohol, yielded colourless prisms, m.p. 187°.

It is fairly soluble in chloroform, sparingly so in acetic acid, ethyl alcohol, acetone, toluene, ethyl acetate, nitrobenzene, and carbon bisulphide, but nearly insoluble in light petroleum, carbon tetrachloride and ether. (Found : Cl, 11·44. $C_{17}H_{17}O_2N_2Cl$ requires Cl, 11·2 per cent.)

This chloro-compound was prepared by West (*J. Chem. Soc.,* 1922, **121**, 2196) by direct chlorination of the amide.

Chloromalon-di-α-naphthylamide dichloride·

This compound was prepared from malon-di-α-naphthylamide (2 g.) and sulphuryl chloride (2·5 g.) in the usual way. The mass obtained, when crystallised from benzene, gave pure shining cubic crystals, m.p. 182°.

It is fairly soluble in chloroform and nitrobenzene, sparingly so in benzene, alcohol, acetone, toluene, acetic acid and ethyl acetate, but nearly insoluble in light petroleum, carbon tetrachloride, carbon bisulphide and ether. (Found : Cl, 23·41. $C_{23}H_{15}O_2N_2Cl_3$ requires Cl, 23·23 per cent.)

Chloromethyl-chloromalondiphenylamide.

The above substance was prepared from methylmalondiphenyl-amide (2 g.) and sulphuryl chloride (2 g.) in the usual way. The solid was precipitated from a large quantity of petroleum. On crystallisation from a small amount of benzene, it gave shining pearly plates, m.p. 128°.

It is fairly soluble in acetone, ethyl acetate, chloroform, ether and nitrobenzene, sparingly so in benzene, alcohol, toluene, acetic acid, carbon tetrachloride and carbon bisulphide, but almost insoluble in light petroleum. (Found: Cl, 21·18. $C_{16}H_{14}O_2N_2Cl_2$ requires Cl, 21·05 per cent.)

Chloromethyl-chloromalon-di-o-tolylamide.

This compound was obtained from methylmalon-di-o-tolylamide (2 g.) and sulphuryl chloride (2 g.) as above. The white solid, on crystallisation from a benzene-petrol mixture, gave a feathery mass, m.p. 130°.

It is fairly soluble in acetone, ethyl acetate and nitrobenzene, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, carbon bisulphide and ether, but insoluble in light petroleum. (Found: Cl, 19·83. $C_{18}H_{18}O_2N_2Cl_2$ requires Cl, 19·43 per cent.)

Chloromethyl-chloromalon-di-p-tolylamide.

The above compound was obtained as shining white needles, when methylmalon-di-p-tolylamide (2 g.) and sulphuryl chloride (2 g.) were made to react in the usual way. It was recrystallised from benzene, in which it is sparingly soluble: m.p. 138°.

The solubility of the chloride was of the same order as the preceding chloride. (Found: Cl, 19·81. $C_{18}H_{18}O_2N_2Cl_2$ requires Cl, 19·43 per cent.)

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Preliminary Note on the Action of *cyclo*-Hexene Oxide on Alkali and Ammonium Halides.

By Hemendra Kumar Sen and Chittaranjan Barat.

In the course of a fermentative experiment, it was found necessary to treat an aqueous suspension of *cyclo*-hexene oxide with a saturated solution of ammonium chloride. The aqueous layer was noticed to have acquired slight alkalinity to litmus and in the course of two days the layer of *cyclo*-hexene oxide settled to the bottom. By this time the alkalinity had developed to such an extent that the ammonium chloride solution could be titrated with N/10 or N/100 sulphuric acid with methyl orange as indicator. The oxide (0·93 g.) and ammonium chloride (53·5 g.) made up to 220 c.c. by water and a few c. c. of alcohol, gave a closely agreeing constant for a pseudo-monomolecular reaction, the mean value of which was 0·116 at 34°. The proportions were 1 mol. of *cyclo*-hexene oxide to 100 mols. of ammonium chloride. The percentage of conversion of *cyclo*-hexene oxide into chlorhydrin was found at equilibrium to be about 80.

It was thought that probably the slight basicity of *cyclo*-hexene oxide was responsible for the alkalinity developed in ammonium chloride solution, but on treating a strong neutral solution of KCl KBr or KI with a few drops of *cyclo*-hexene oxide as above, the alkalinity developed readily in a few minutes in the order, KI, KBr, KCl. The development of free KOH in potassium halide solutions can be demonstrated by adding a drop or two of phenolphthalein to the reaction mixture : a pink colour develops which can be discharged with carbonic acid. After a short time the colour reappears showing the further progress of the reaction as explained below.

$$CH_2 < {CH{-}CH \atop CH_2 \cdot CH_2} > CH_2 + KX + H_2O$$

$$\underset{\longleftarrow}{\longrightarrow} CH_2 < {CH_2 \cdot CH_2 \atop CH_2 \cdot CHX} > CHOH + KOH$$
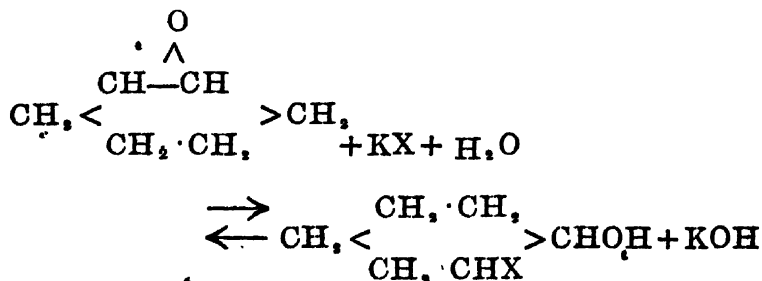
This explanation, however, is tentative.

Pyrylium Salts and *spiro*-Dipyrans. Part I. Condensation Products from *o*-Hydroxy-aldehydes and α-Alkylated β-ketonic Esters.

By Satish Chandra De.

Synthesis of anhydropyranol or pyrylium salts have been investigated by a large number of investigators (Wagner and Bülow, *Ber.*, 1901, **34**, 1195 ; Dilthey, *J. pr. Chem.*, 1904, **70**, 275 ; 1916, **94**, 72; Schneider and Ross, *Ber.*, 1922, **55**, 2775). The methods depend chiefly on the use (i) of a phenol and a substance containing the group, $CHO \cdot CH_2 \cdot CO$ and (ii) of an *o*-hydroxy aldehyde and a substance containing the group $\cdot CH_2 \cdot CO$—.The pyrylium salt is isolated in the form of a ferric or perchloric acid salt. The following examples exhibit the relations between the two methods :
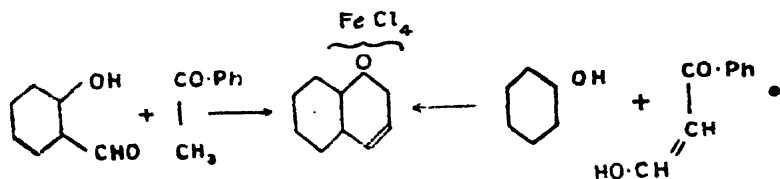
Up till now, *o*-hydroxy-aldehydes have not been condensed with α-alkylated β-ketonic esters, although β-ketonic esters, *e.g.*, aceto- and benzoyl-acetic esters have been condensed with *o*-hydroxy aldehydes to coumarone derivatives (Kostanecki, *Ber.*, 1908, **41**, 1148) using piperidine as the condensing agent. In the present communication, which is of a preliminary character, the author has described the behaviour of *o*-hydroxy-aldehydes towards α-alkylated β-ketonic esters in presence of gaseous hydrochloric acid. It has been found that those ketonic esters containing only one reactive hydrogen atom in the alpha position readily react with the aldehydes to yield highly coloured benzopyrylium salts. In each case two molecules of the aldehyde and one of the ester yield a 3-alkyl-2-(*o*-Hydroxystyryl)-benzopyrylium salt. An unsuccessful attempt was made by the author to prepare a pyrylium compound from aceto-acetic ester and salicylaldehyde in presence of hydrochloric acid,

The reaction product, which had an intensive red colour, did-not respond to the usual properties of pyrylium salts or of coumarones.
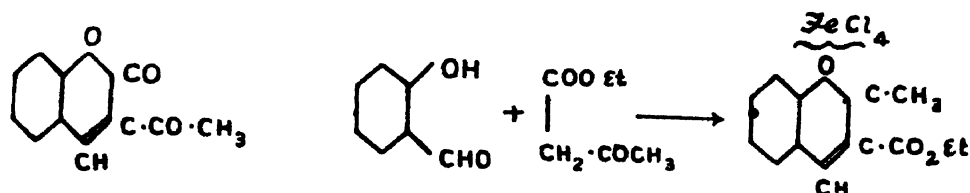
As to the mechanism of the reaction in the formation of pyrylium salts, it is presumed that the first phase of the condensation involves the elimination of the carbethoxy group and the formation of a primary 2:3-dialkylbenzopyrylium salt. The second phase in the condensation depends on the presence of a reactive 2-methyl group (Plancher, *Gazzetta*, 1898, **28**, 417; Dilthey, *Ber.*, 1923, **56**, 1012; Mills, *J. Chem. Soc.*, 1922, **121**, 2724) which condenses with the second molecule of the aldehyde producing 3-alkyl-2-(o-hydroxy styryl-)-benzopyrylium salt. The following example explains the reaction.
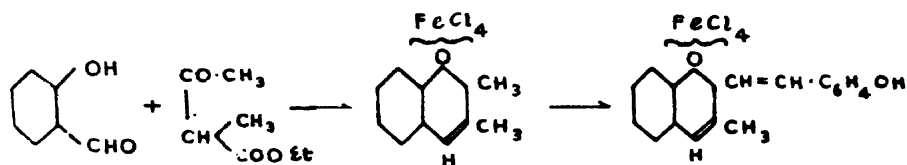
The above explanation for the mechanism finds support from the following observations :—

(i) The pyrylium salt derived from α-methylacetoacetic ester and salicylaldehyde is identical with that prepared from salicylaldehyde and the 2:3-dimethylbenzopyrylium ferric chloride of Decker (*Annalen*, 1909, **364**, 37). (ii) 2-Phenyl-3-methylbenzopyrylium perchlorate obtained from salicylaldehyde and propiophenone by Decker's method is identical with that derived from salicylaldehyde and α-methylbenzoylacetic ester. The close resemblance between the two synthetic methods is thus represented :—
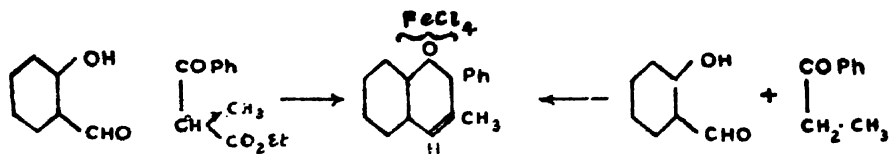
By hydrolytic decomposition of the o-hydroxystyryl benzopyrylium salts, the pseudo bases, 2-hydroxy-2-(o-hydroxystyryl)-α-chromanes could not be isolated; the alcoholic and phenolic hydroxyl

groups react with the elimination of a molecule of water and forma·
tion of *spiro*-dipyrans (Decker, *Ber.*, 1908, **41**, 2997; *Annalen*,
1908, **364**. 37). The *spiro*-dipyrans, which are colourless, are
converted by strong acids into the highly coloured hydroxystyryl
benzopyrylium salts. The cycle of changes is represented below.
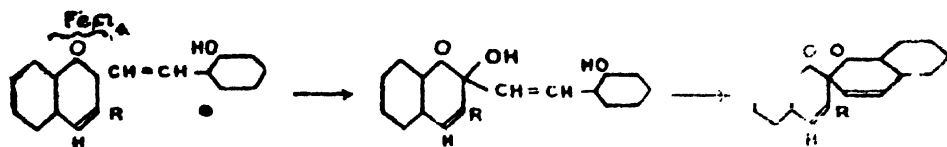
<div align="center">EXPERIMENTAL.</div>

3-*Methyl*-2-(o-*hydroxystyryl*)-*benzopyrylium chloride*.

A mixture of salicylaldehyde (2 mols.) and α-methylacetoacetic
ester (1 mol.) was diluted with dry ether and dry hydrogen chloride
gas was passed into the ethereal solution, cooled by ice, for 2 to
3 hours. The deep coloured crystals that separated were filtered,
washed with ether and dried in a vacuum. It was obtained in deep
red needles having a coppery lustre, m.p. 200°. (Found : C, 72·53 ;
H, 5·26. $C_{18}H_{15}O_2Cl$ requires C, 72·36 and H, 5·03 per cent.)

3-*Methyl*-2-(o-*hydroxystyryl*)-*benzopyrylium ferric chloride*.—
(a) The pyrylium chloride was dissolved in glacial acetic acid
and to this was added an acetic acid solution of ferric chloride. The
ferric salt separated as a red flocculent precipitate which, when
crystallised from acetic acid, was obtained in red needles, m.p. 180°.
(b) 2 : 3-Dimethylbenzopyrylium ferric chloride (Decker, *loc.
cit.*) was heated with salicylaldehyde in acetic acid solution. On cool-
ing and allowing to stand, the ferric salt separated in long needles;
it was washed with ether and dried, m.p. 180°. (Found : C, 47·17 ;
H, 3·51. $C_{18}H_{15}O_2FeCl_4$ requires C, 46·85 ; H, 3·25 per cent).

3-*Methyl*-2-(o-*hydroxystyryl*)-*benzopyrylium perchlorate* was
obtained by adding perchloric acid to the pyrylium chloride dissolved
in acetic acid. The deep red crystals that separated were filtered,
washed with acetic acid and then with ether, m.p. 244°. (Found :
C, 59·69 ; H, 4·35. $C_{18}H_{15}O_6Cl$ requires C, 59·57 ; H, 4·19 per
cent.)

3-*Methyl*-spiro-*dibenzopyran*.

∴ The decomposition of the above ferric salt was effected
in the following way. The salt was intimately mixed with
anhydrous sodium acetate and the mixture was suspended

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in ether to which strong ammonia solution was added drop by drop. The mixture was frequently shaken and the addition of ammonia was continued till the colour of the ferric salt disappeared. The reaction product, which remained in solution, was filtered from ferric hydroxide and was obtained in crystals on the evaporation of the ether. Purified by crystallisation from petroleum ether, it was obtained in white needles, m.p. 80°. (Found: C, 81·73; H, 5·91. $C_{18}H_{14}O_2$ requires C, 82·01; H, 5·70 per cent.)

It is soluble in alcohol, benzene and ether; difficultly soluble in petroleum ether. From the colourless solution the pyrylium compound is precipitated as the ferric salt by means of hydrochloric acid and ferric chloride.

3-*Benzyl*-2-(o-*hydroxystyryl*)-*benzopyrylium chloride.*—a-Benzyl-acetoacetic ester (1 mol.) and salicylaldehyde (2 mols.) were mixed with dry ether and dry hydrochloric acid gas was passed as in the previous case. The highly coloured solution was allowed to stand and after two days the crystals that separated in dull red needles were filtered, washed with ether and dried. It crystallised from acetic acid as red needles, m.p. 129°. (Found: C, 77·11; H. 5·23. $C_{24}H_{19}O_2Cl$ requires C, 76·90; H, 5·07 per cent.)

3-*Benzyl*-2-(o-*hydroxystyryl*)-*benzopyrylium ferric chloride* was obtained by adding ferric chloride to the pyrylium chloride dissolved in acetic acid. The ferric salt separated in red needles which, after crystallisation from acetic acid, had m.p. 194°. (Found: C, 53·81 ; H, 3·76. $C_{24}H_{19}O_2FeCl_4$ requires C, 53·63; H, 3·53 per cent.)

3-*Benzyl*-2-(o-*hydroxystyryl*)-*benzopyrylium perchlorate* was prepared by adding perchloric acid to the pyrylium chloride solution of acetic acid. The red crystals were filtered, washed with ether and dried, m.p. 234°. (Found: C, 65·91; H, 4·45. $C_{24}H_{19}O_6Cl$ requires C, 65·66; H, 4·37 per cent.)

3-*Benzyl*-spiro-*dibenzopyran* was obtained by the decomposition of the above perchloric acid salt by the method already used. The crystals obtained by the evaporation of the ether were dissolved in benzene with the addition of animal charcoal, and from the solution on concentration the benzyl-*spiro*-dibenzopyran was obtained, m.p. 126°. (Found: C, 85·41; H, 5·64. $C_{24}H_{18}O_2$ requires C, 85·17; H, 5·36 per cent.)

It is insoluble in petroleum ether and easily soluble in ether, benzene and alcohol. From the colourless solution the pyrylium compound is obtained as its ferric salt by hydrochloric acid and ferric chloride.

3-Methyl-2-(o-hydroxy-a-benzostyryl)-β-naphthopyrylium ferric chloride.—β-Naphthol-a-aldehyde (2 mols.) was dissolved in glacial acetic acid and to the solution a-methylacetoacetic ester (1 mol.) was added and the mixture, after saturation with hydrochloric acid gas with cooling, was kept overnight after which it was warmed on the water-bath for several hours. The deep coloured crystals, that separated from the solution of the pyrylium chloride on the addition of ferric chloride, were filtered, washed with acetic acid and finally with ether. (Found: C, 55·84; H, 3·56. $C_{26}H_{19}O_2FeCl_4$ requires C, 55·61; H, 3·38 per cent.)

3-Methyl-2-(o-hydroxy-a-benzostyryl)-β-naphthopyrylium perchlorate was prepared by adding perchloric acid to the solution of the pyrylium chloride. The crystals were filtered and crystallised from acetic acid; m.p. above 308°. (Found: C, 67·28 ; H, 4·27. $C_{26}H_{19}O_6Cl$ requires C, 67·43; H, 4·15 per cent.)

3-Methyl-spiro-2 : 2'-di(β-naphthyl-5 : 6-pyran-1 : 2) was obtained from the above ferric salt in the usual way using benzene in which it is soluble. The benzene solution was filtered from solids and boiled with animal charcoal; and from the filtrate on concentration colourless crystals were obtained, m.p. 200°. (Found: C, 86·33 ; H, 5·28. $C_{26}H_{18}O_2$ requires C, 86·15 ; H, 5·02 per cent.)

The *spiro*-dipyran is insoluble in ether and petroleum ether; readily soluble in hot benzene or toluene. The colourless solution, on boiling, assumes a blue-violet colour which disappears on cooling. From the colourless solution the pyrylium salt is again obtained as its ferric salt by adding hydrochloric acid and ferric chloride.

3-Benzyl-2-(o-hydroxy-a-benzostyryl)-β-naphthopyrylium ferric chloride was obtained from β-naphthol-a-aldehyde (2 mols.) and a-benzylacetoacetic ester (1 mol.) in glacial acetic acid solution which was saturated with hydrochloric acid gas with cooling. The mixture was then warmed on the water-bath for several hours. From the pyrylium chloride solution the ferric salt was precipitated by ferric chloride; the crystals were filtered, washed with acetic acid and ether, and dried. (Found: C, 94·12 ; H, 5·88. C $H_{23}O_2FeCl_4$ requires C, 94·35 ; H, 5·65 per cent.)

3-Benzyl-2-(o-hydroxy-a-benzostyryl)-β-naphthopyrylium perchlorate was prepared by adding perchloric acid to the acetic acid solution of the pyrylium chloride. The crystals were filtered, washed with ether and dried, m.p. 204°. (Found: C, 71·50 ; H, 4·22. C_{2} $H_{23}O_6Cl$ requires C, 71·28 ; H, 4·31 per cent.)

*3-Benzyl-*spiro-2 : 2'-*di(β-naphtho-5 : 6-pyran-*1 : 2).—The above ferric salt was decomposed as before. The benzene solution was boiled with animal charcoal, filtered and to the filtrate petroleum ether was added when the *spiro*-dinaphthopyran separated in colourless crystals, m.p. 205°. (Found: C, 87·88 ; H, 5·46. $C_{31}H_{22}O_2$ requires C, 87·64 ; H, 5·78 per cent.)

2-Phenyl-3-methyl-benzopyrylium perchlorate.—(a) A mixture of α-methylbenzoylacetic ester (1 mol.), salicylaldehyde (1 mol.) and perchloric acid (1 mol.) was diluted with ether and the ethereal solution saturated with hydrochloric acid gas. The mixture was allowed to stand when the orange coloured crystals gradually separated. After two days these were filtered, washed with ether and crystallised from acetic acid in orange needles, m.p. 179°.

(b) Propiophenone (1 mol.), salicylaldehyde (1 mol.) and perchloric acid (1 mol.) were dissolved in ether and through the ethereal solution hydrochloric acid gas was passed. The orange needles that separated were crystallised from acetic acid ; m.p. 179°. (Found: C, 59·68 ; H, 4·28. $C_{16}H_{13}O_5Cl$ requires C, 59·87 ; H, 4·08 per cent.)

A benzopyrylium salt has been obtained from salicylaldehyde and methylethylketone identical with that prepared from salicylaldehyde and α-methylacetoacetic ester. This part of the work will be described in a subsequent paper.

Protective Action of Rochelle Salt on Cupric Oxide Sol. Part I.

By S. K. Basu and M. Lakshmanan.

The stabilising action of electrolytes on sols is well known, and instances of protection by ions of higher valency are also common where protection is preceded by a reversal of charge on the colloid. Friedemann and Neisser (*Munich Medical Weekly,* 1903, No. 11, 51) as well as Bechold (*Zeit. physical, Chem.,* 1904, **48**, 385) were the first to observe this reversal of charge on hydrophobe sols. Buxton and Teague (*Zeit. physikal. Chem.,* 1907, **57**, 64, 76) in the case of platinum sols and ferric chloride, Kruyt and van der Speck (*Koll. Zeit.,* 1919, **25**, 17) in the case of negative ferric oxide sol and disodium hydrogen phosphate, and Powis (*J. Chem. Soc.,* 1915, **107**, 818) also in the case of negative ferric oxide sol have studied this reversal of charge in a quantitative manner.

The following is an attempt to study the coagulation by an electrolyte of a sol the charge on which has already been reversed by another electrolyte. Thus cupric oxide sol prepared by Bredig's method was treated with varying concentrations of Rochelle salt, when reversal of charge was found to occur and the sol found to be rendered alkaline and more stable. If the concentration of the Rochelle salt in the mixture is well above 0·003 millimoles per litre the charge-reversal takes place without any previous coagulation.

Experimental.

The cupric oxide sol was prepared by the electrical dispersion method of Bredig. The electrodes were of pure electrolytic copper wires of 2 mm. thickness and six to seven inches in length. The make and break between them was secured by the use

of a light electric motor which kept one of the electrodes in constant vibration. (Paine, *Kolloidchem. Beihefte*, 1913, **4**, 16.)

The spark-gap was about 1 mm. and a current of 8 amperes at 65 volts was used. Water redistilled in silica vessels and stored up in Jena glass vessels was used as the medium.

The light green sparks between the electrodes generated, after about fifteen minutes, a light green liquid, and as the sparking continued, the colour deepened till after an hour's sparking a brown liquid resulted. Thus every time a 500 c.c. Jena beakerful of sol was obtained, which, after settling, was stored in a large hard glass bottle for the following experiments. The amount of copper was determined iodometrically by means of thiosulphate and was found to be 0·0392 gm. of copper per litre.

The coagulation values of sodium sulphate for the pure sol as well as for the sol protected by different concentrations of Rochelle salt were found in the usual manner, keeping the volume constant in each case. The time allowed for the precipitation was three hours. A difference between the coagula of the unprotected and protected sols was noticeable: the coagulum of the protected sol consisted of particles much finer than those of the other.

The protected sol could also be reduced by glucose and hydrogen peroxide, etc., to an unstable cuprous oxide sol with a red-green fluorescence. Also, when the Rochelle salt was particularly dilute, e.g., 0·003 millimoles per litre, it no longer protected the sol but coagulated it.

Table I shows the relation between the concentration of Rochelle salt employed for protection and the corresponding coagulation values for sodium sulphate. These results could be repeated and a fair agreement obtained. Fig. 1 exhibits the relation between the concentration of Rochelle salt and the corresponding coagulation values for sodium sulphate and Fig. 2 illustrates the relation between the logarithms of the said quantities.

That the protection afforded was due to reversal of charge was verified by coagulating the protected sol with sodium sulphate and calcium sulphate. The coagulation values are given in Table II.

Another important fact observed was that when the concentration of Rochelle salt in the sol was greater than 800 millimoles per litre, the sol began to dissolve, there resulting in about 12 hours' time a blue-green solution.

TABLE I.

Rochelle salt in millimoles per litre.	Coagln. values for Na₂SO₄ in millimoles per litre.
nil	0·123
0·017	0·187
0·033	0·461
0·042	0·636
0·050	0·772
0·067	1·155
0·084	1·534
0·167	4·036
0·251	7·6.5
0·334	11·550
0·501	17·330
0·668	26·720
0·835	36·870
1·002	48·140
1·253	77·060

TABLE II.

Concn. of Rochelle salt (millimoles per litre)	Coagulation value of Na in millimoles per litre.	Coagulation value of Ca in millimoles per litre.
0·6667	53·34	1·76

Since Rochelle salt is optically active and the sol itself inactive, its adsorption by the latter was next investigated with the polarimeter. To 10 c.c. of sol a known volume of standard Rochelle salt was added and the total volume made up to 50 c.c. with distilled water. Rochelle salt solution as in above was next made up to 50 c.c. with distilled water alone. The rotations given by these were compared. By increasing the volumes of the standard Rochelle salt. solution by stages eight sets of rotations with and without sol were

taken. *The rotations were observed with a two-decimetre tube ; the* source of illumination was an electric arc, the light from which was rendered monochromatic by a dichromate filter. As the arrangement was not very sensitive, sufficient reliance cannot be placed on these results.

The polarimetric readings were interpreted as follows. The rotation obtained with the sol to which Rochelle salt was added was assumed to be proportional to the equilibrium concentration, and the difference between this and the rotation given by pure Rochelle salt of the same concentration was taken as being proportional to the amount adsorbed.

The results obtained are tabulated below, the graphs showing the relation between the equilibrium rotation and the amount adsorbed, as also that between the logarithms of the two quantities are given in Figs. 3 and 4.

<div align="center">TABLE III.</div>

Rotation of the equln. concn. of Rochelle salt.	Rotn. cong. amt. adsorbed
0·22°	0·01°
0·34°	0·02°
0·53°	0·03°
0·68°	0·04°
0·81°	0·05°
1·02°	0·07°
1·16°	0·08°,
1·35°	0·11°

In the above experiments care was taken not to let the concentration of the Rochelle salt overstep the limit where it dissolves the sol in course of time.

To make a closer study of this phenomenon of protection, experiments on absorption spectra were tried. On the addition of Rochelle salt to the sol, a slight change as regards transparency was observable—perhaps due to a change in the size of the particles— and this induced the attempt. The absorption spectra were photographed both in the ultraviolet as well as in the visible region.

Since on the addition of Rochelle salt to the sol no characteristic change was deducible from photography in the ultraviolet, attention

was turned to photography in the visible region. The constant-deviation spectrometer of Adam Hilger was used with Kodak's special rapid panchromatic films.

No perceptible distinction between the spectra of the sol with and without Rochelle salt was noticeable, both in the ultraviolet and the visible spectrographs.

Surface tension and viscosity measurements of the unprotected and protected sols were also made. But the results obtained did not characterise any difference ; so that no fresh light could be obtained from these experiments.

Conductivity measurements, however, go to show that the sol containing a known small concentration of Rochelle salt is more conducting than conductivity water containing the same concentration of the salt.

TABLE IV.

Conc. of Rochelle salt.	Conductivity in reciprocal ohms.	
	In water	In sol
8·75 mm. per litre.	0·0291	0·0298

That protection is preceded by a charge-reversal was conclusively established by cataphoretic experiments. The pure sol began to clear away from the anode in about 2 to 3 minutes and to rise in the cathode limb. On the other hand, the protected sol which contained 80 millimoles of Rochelle salt per litre took about fifteen minutes before it began to wander away from the cathode. Thus while the pure sol is positively charged, the protected sol carries a negative charge.

Discussion.

As a consequence of reversal of charge one should differentiate between two coagulation values, a lower one corresponding to the original sol and a higher one corresponding to the reversed sol. There is hardly any doubt that a reversed sol is quite a different sol from the original one, and for its coagulation, it is again the oppositely charged ions that are responsible according to their adsorbability and valency. Extensive work in this direction is lacking : but a few measurements of Friedemann and Neisser (*loc. cit.*) show it

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distinctly. They showed that the coagulation values of matrix sol reversed by ferric chloride and aluminium sulphate are ˙60 millimoles and 1˙7 millimoles per litre respectively. This corresponds to the big difference in coagulation values of chlorine ions and sulphate ions for positive sols.

Instead of taking the same electrolyte for reversal of charge and subsequent coagulation, different electrolytes were taken, *i.e.*, Rochelle salt and sodium sulphate. The stabilising action of Rochelle salt was shown to be limited, however, by two factors. In very small concentrations, it coagulates the sol; and in fairly large concentrations it dissolves the copper oxide and presents a slightly alkaline and light blue solution. In the intermediate concentrations, it has been shown that progressively increasing protection is afforded by larger and larger concentrations of Rochelle salt used ; the coagulation values of the electrolyte sodium sulphate go on increasing with increasing concentrations of the protective agent between the limits (*a*) of coagulation at the first critical potential and (*b*) of solution by the latter.

It is well known that organic ions show generally greater adsorbability than simple inorganic ions. If the organic ion in question, besides being highly adsorbable, has a high valency a reversal of charge is what is to be expected. Such is the case with the tartrate ion with respect to copper oxide. It is evident from the data given (Table I, Figs. 1 and 2) that the adsorption of Rochelle salt by copper oxide sol increases with the concentration of the former. If it is assumed that at the coagulation point the charge on the protected sol is lowered to a minimum value, namely, the first critical potential of Powis, then this lowering is brought about, no doubt, by the adsorption of the alkali ion. If a further assumption is now made that owing to the very dilute nature of the sol and the dilute nature of the protective electrolyte contained in it, the amount of an ion adsorbed is small compared to the amount of electrolyte added, then Freundlich's isotherm may be written as

$$a = KC^{\frac{1}{n}}$$

where *a* is the amount adsorbed and C, the amount of electrolyte added. This, of course, is a first approximation. The tartrate adsorption may thus be expressed by

$$a_t = KC_t^{\frac{1}{n}}$$

where a_t is the amount of tartrate ion adsorbed against C_t the concentration added.   Similarly

$$a_{Na} = K_1 C_{Na}^{\frac{1}{n}}$$

will express the relation between the amount of alkali ion adsorbed and the concentration of sodium sulphate added.   Assuming then . an equivalence in adsorption between the tartrate ion and the coagulating sodium ion, at the point of coagulation

$$KC_t^{\frac{1}{n}} = K_1 C_{Na}^{\frac{1}{n}}$$

so that if the coagulation values for sodium sulphate are plotted against the Rochelle salt concentration, Freundlich's adsorption isotherm ought to result.   That it is so is borne out by Fig. 2. That the adsorption of tartrate follows Freundlich's isotherm is further shown by the results obtained from polarimetric measurements as given in Table III (Fig. 4).   It is remarkable, however, that the curves (Figs. 1 and 3) bend towards the adsorption axis instead of the concentration axis as is generally the case, and yet Freundlich's adsorption isotherm is obeyed.

The lack of any definite results from absorption spectra both in the visible and ultraviolet regions may be partly due to the defect in the source of light, whose intensity could not be controlled and maintained constant, even for the short time of exposure, and partly to the very dilute nature of the sol which was subjected to . these investigations.   A characteristic difference in spectra was indeed once obtained which, however, could not be repeated.

It has been previously stated that Rochelle salt protects copper oxide sol between certain limits.   At the lower one coagulation occurs and at the higher solution takes place.   The process of solution near about this higher limit is a slow one and no sudden change is brought to light.   It follows clearly from this that adsorption is merely the first stage in chemical action.   When the tartrate ions are preferentially adsorbed by the copper oxide particles, hydroxyl ions make their appearance in solution, and when these reach a certain concentration, probably a readjustment in the forces of valency occurs, and a new compound is formed.   The nature of this new compound has been the subject of study of the next part.   It appears also that the presence of hydroxyl ions is

necessary for the formation of the new blue compound, and a limiting value for such concentration can be laid down.

One is indeed tempted to ascribe the protective action to the formation of a second colloid within the first. During the process of sparking, copper oxide particles, some copper ions and hydroxyl ions are formed. Of these, the copper oxide particles adsorb the less mobile copper ions, thus forming a positively charged sol, with a surrounding second layer of hydroxyl ions. When Rochelle salt is added the tartrate ion is adsorbed in excess forming negatively charged colloidal copper tartrate and displacing the hydroxyl ions. These in turn react with the copper tartrate forming a soluble basic tartrate ; thus results the blue liquid for the higher limit of the Rochelle salt concentration.

Summary.

(1) The protective action of Rochelle salt on copper oxide sol was studied ; a relation between the protecting power and the concentration of protective agent was obtained on the basis of the coagulation values of the protected sol. Thus the coagulation values for sodium sulphate were found to increase with the concentration of Rochelle salt employed as a protective agent. When the logarithms of the coagulation values are plotted against the logarithms of concentrations of Rochelle salt used, a straight line was obtained.

(2) The adsorption of Rochelle salt by the sol was further studied with the polarimeter and Freundlich's relation was found to hold.

(3) The curves obtained showing the relation between concentration and adsorption were found to be bent away from the concentration axis, unlike the ordinary isotherms.

(4) A comparison of the absorption spectra of the protected and the pure sol was made by taking photographs both in the visible and ultraviolet regions.

(5) Cataphoretic experiments showed that the protection by Rochelle salt was due to a reversal of charge.

(6) A mechanism of protection and coagulation has been suggested.

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ROCHELLE SALT IN MILLIMOLES PER LITRE.

FIG. I.

LOGS OF ROCHELLE SALT CONC'N.

FIG. II.

ROTATION OF EQLM. CONCN. OF ROCHELLE SALT
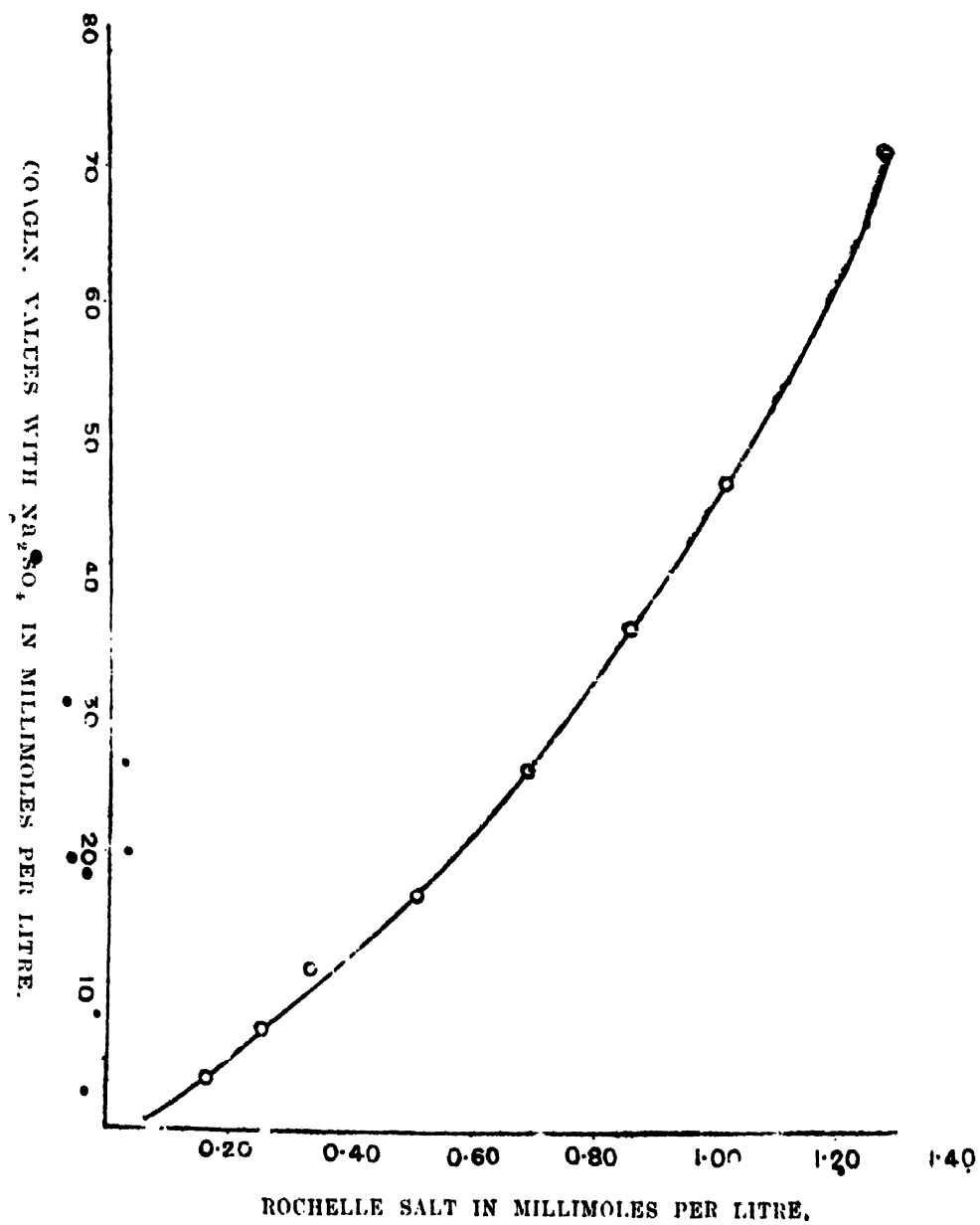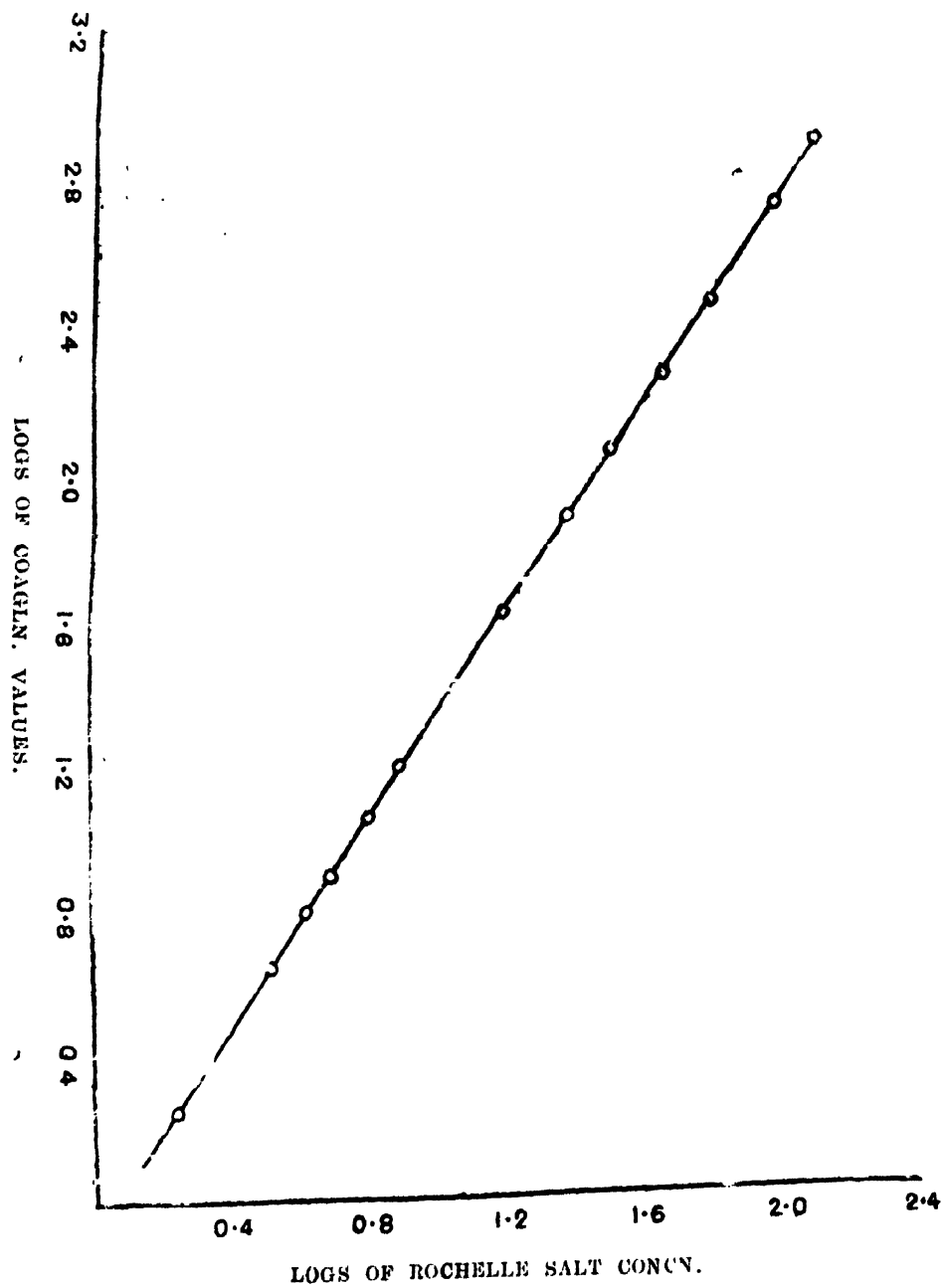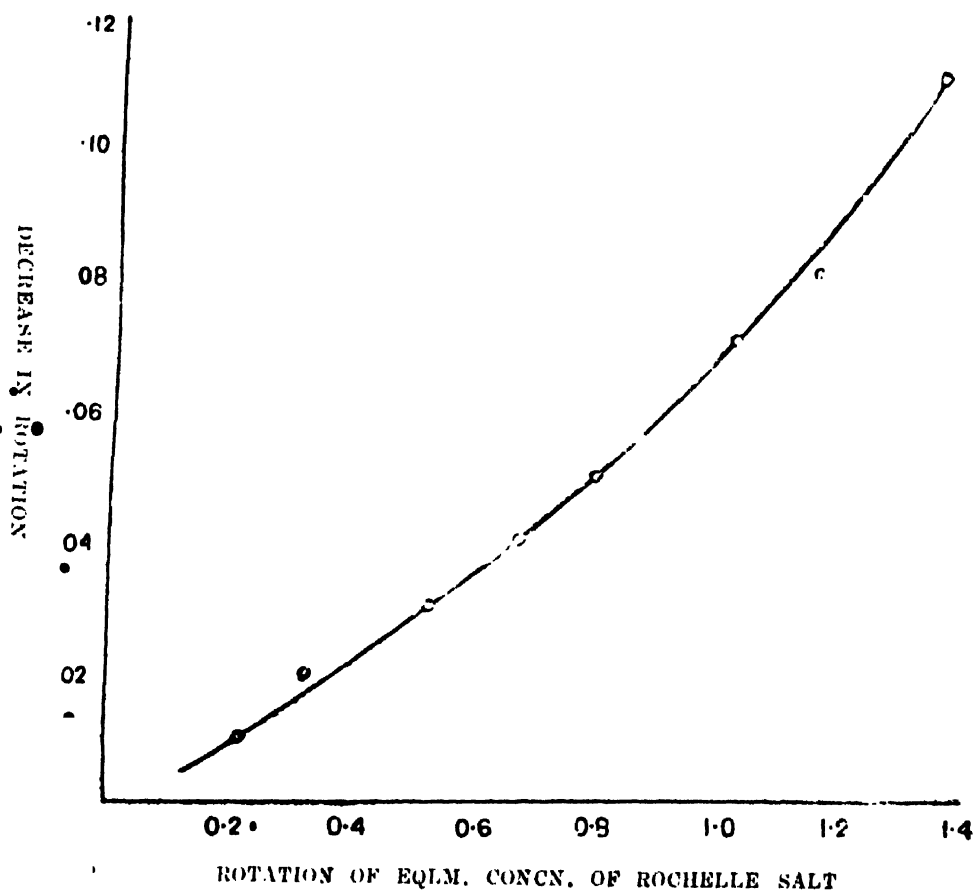
FIG. III.
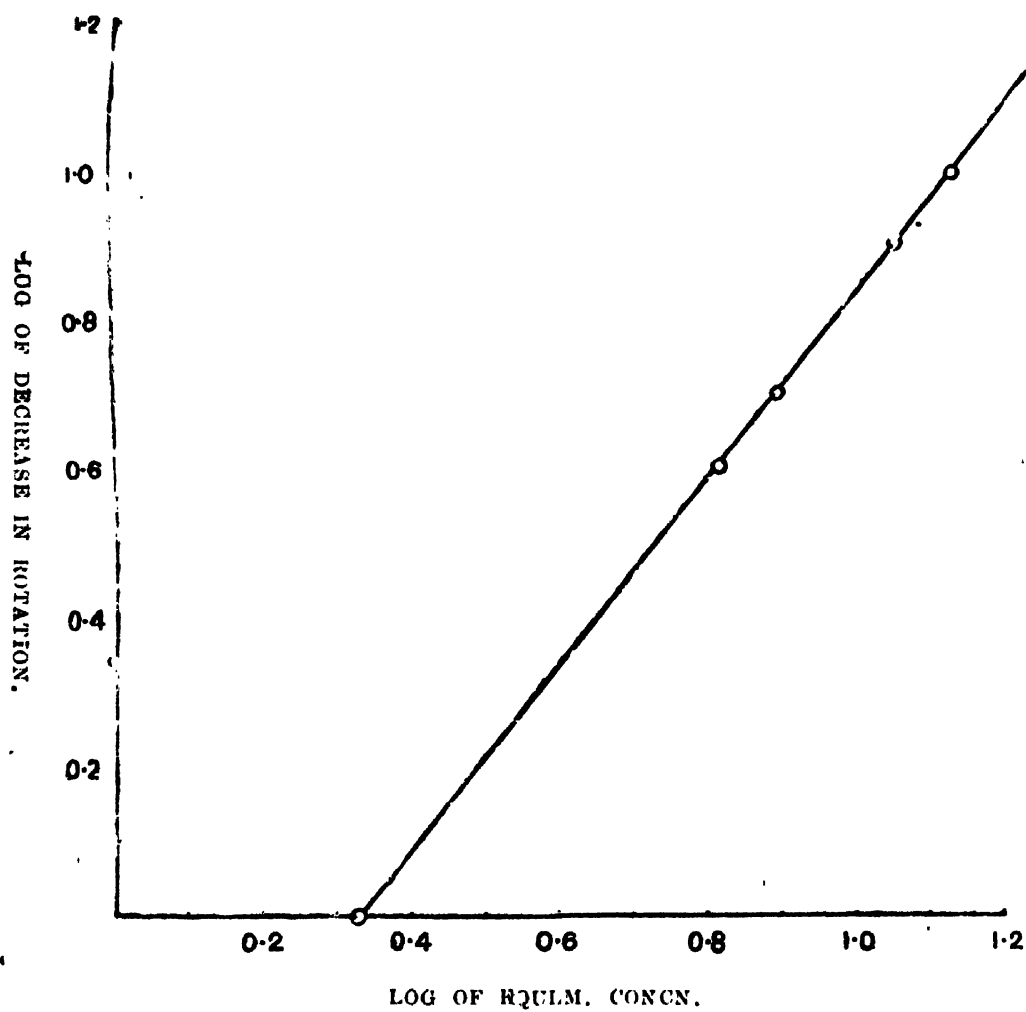
FIG. IV.

On a New Series of Double Sulphates of the Copper-Magnesium Group and the Sulphonium Bases. Part I.

By Prafulla Chandra Ráy and Nirmalendunath Ráy.

Sulphonium compounds have long been known. The starting point of preparing the various sulphonium compounds is generally the sulphonium iodide which is obtained by the condensation of a sulphide with an alkyl iodide. Thus triethyl sulphonium iodide is obtained according to the reaction,

$$(C_2H_5)_2S + C_2H_5 \cdot I = (C_2H_5)_3S \cdot I.$$
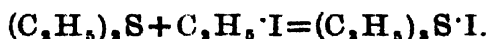
By far the more important compound of this class is the hydroxide which is obtained by treatment of the iodide with moist silver oxide. The sulphonium hydroxides have been found to be strong bases and are comparable to the hydroxides of the alkali metals, the l eats of neutralisation and other physico-chemical data of these two classes of bases being very nearly the same. It thus appears that the corresponding salts of the sulphonium compounds will be well-defined crystalline salts and will behave similarly to the salts of the alkali metals. Now, it is a well known fact that the simple salts of the alkali metals form double salts with the salts of various metals such as mercury, gold, platium, cadmium, iron, copper, etc. The sulphonium salts are, therefore, likely to produce such double salts. In fact Stromholm (*Ber.*, 1898, **31**, 2283) has obtained double salts of sulphonium chlorides with mercuric chloride. Klinger and Massen have obtained double salts of sulphonium chlorides and iodides with iodides of cadmium, mercury, platinum, gold, tin and arsenic. (*Annalen*, 1888, **243**, 193; 1889, **252**, 241). Blattler (*Monatsh*, 1919, **40**, 417) has obtained double salts of trimethyl sulphonium halides with metallic halides.

Uptil now no double sulphate has been obtained from the sulphonium sulphates and other metallic sulphates. It is well known that

sulphates of certain bivalent metals yield, as a rule, with alkali sulphates as also with the sulphate of ammonia, double salts of the type,

$M''SO_4 \cdot M'_2SO_4 \cdot 6H_2O$,   where
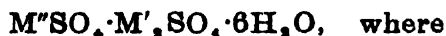
M'' = Fe (ous), Ni, Co, Zn, Mn, Mg, Cu, Cd, etc.,

and M' = K, Na, (NH_4), etc.

Sulphates derived from strong organic bases are also known to form double salts with these metallic sulphates and are either exactly or very similar to the type mentioned. Thus Grossman and Schuck (*Z. anqrg. Chem.*, 1906, **50**, 27; *Chem. Zentr.*, 1906, **II**, 1048, 1243) describe a double sulphate of ethylamine sulphate and zinc sulphate, $(C_2H_5NH_2)_2H_2SO_4 \cdot ZnSO_4 \cdot 8H_2O$ and Grossman, Schuck and Steinmetz (*Z. anorg. Chem.*, 1906, **50**, 29; *Chem. Zentr.*, 1905, **II**, 1048, 1243) described the double salt $(CH_3NH_2)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$. With ethylene diammonium sulphates of the above bivalent metals Grossman and Schuck (*loc. cit.*) have also obtained double sulphates containing four, six, and eight molecules of water of crystallisation. Recently similar double sulphates have been obtained by Canneri (*Gazzetta*, 1925, **55**, 611) from guanidine sulphate and these metallic sulphates in which case the salts are of the type $M''SO_4 \cdot M'_2SO_4 \cdot 6H_2O$. In all these double salts it is found that the organic sulphates behave like sulphates of the alkali metals. It was, therefore, expected that sulphonium sulphates will also behave similarly. Consequently it was found desirable to study the interaction of the sulphates of the sulphonium bases with the vitriolic sulphates.

The expectation has been only partially realised. Double sulphates of triethyl sulphonium sulphate and the vitriolic sulphates have been obtained with this difference that instead of being hexa-hydrated as was anticipated from the close analogy of the sulphonium compounds with those of the alkali metals, they are invariably deca-hydrated. The behaviour of manganese and magnesium has been, however, found to be rather anomalous, as the double salts, which they yield, conform to the formula $2\,M''SO_4 \cdot M_2SO_4$, $11H_2O$. Double sulphates of manganese and ammonium (Lepierre, *Compt. rend.*, 1895, **120**, 924; *Bull. Soc. Chim.* 1895, [iii] **13**, 595; Schreinemakers, *Chem. Weekblad*, 1909, **6**, 131), manganese and potassium (Mallet, *Chem. News*, 1899, **80**, 300) and also of magnesium and potassium (Precht, *Chem. Industrie*, 1880, **3**, 418)

and of magnesium and sodium (Chatelier, *Compt. rend.*, 1896, **123**, 746) of the type $2M''SO_4$, M'_2SO_4 have been described but they contain no water of crystallisation, whereas those which form the subject of the present investigation contain eleven molecules of water.

Sulphonium sulphates have not yet been isolated and in the present case it has been found that on neutralising the triethyl sulphonium hydroxide with sulphuric acid, the sulphate can be obtained in solution only. On being concentrated and finally evaporated to dryness in a vacuum it solidifies to a transparent glassy mass, which on being exposed to the moist atmosphere absorbs moisture and in a few minutes goes into solution. It was thus too hygroscopic to admit of direct weighing. It was also soluble in alcohol, as is expected in the case of an organic sulphate. In these respects, therefore, the sulphonium sulphates behave differently from the sulphates of the alkali metals. The strong affinity of the sulphonium compounds for water, exhibited by their hygroscopic nature, seem to be satisfied by a large water content of the molecule of the derived double sulphates.

These double sulphates are hygroscopic and crystallise in needles. They are readily soluble in water and when their concentrated aqueous solutions are treated with alcohol, the inorganic components alone separate out. On heating on a platinum spatula, the substances melt in the water of crystallisation and afterwards decompose with charring; the organic sulphur component is found to burn on the spatula and a smell of ethyl sulphide is distinctly perceptible.

One remarkable behaviour was observed when, in the case of nickel, methyl sulphonium sulphate was substituted for the corresponding ethyl derivative. The double salt obtained had the formula $2NiSO_4,[(CH_3)_3S]_2SO_4, 11H_2O$, that is, it behaved like manganese and magnesium sulphates.

EXPERIMENTAL.

Preparation of Triethyl Sulphonium Sulphate.

The method given by Oefele (*Annalen*, 1865, **132**, 82) for the preparation of the iodide is lacking in detail. The following procedure gave satisfactory results.

Thirty-two g. of ethyl iodide and 18 g. of ethyl sulphide with 10 c.c. of water were heated under reflux on a water bath for 15 to

20 hours till a homogeneous solution was obtained. The solution which was coloured by the liberated iodine was allowed to evaporate spontaneously in a vacuum, when colourless rhombic plates of triethyl sulphonium iodide crystallised out in two or three days (yield about 40 g.). The iodide may be purified by recrystallisation from hot anhydrous alcohol or from a mixture of anhydrous alcohol and ether.

The iodide was then converted into the hydroxide by rubbing with excess of silver oxide in presence of water. The solution was filtered, the filtrate neutralised with dilute sulphuric acid and concentrated somewhat on the water-bath. As it cannot be isolated, the preparations of the double salts had to be undertaken with the sulphonium sulphate in solution.

General Method for the Preparation of the Double Sulphates.

Considerable difficulty was experienced in preparing the double salts. The reactant sulphates were at first mixed in molecular proportions, the amount of the sulphonium sulphate being calculated from the amount of the iodide taken, and the solution was allowed to evaporate spontaneously over sulphuric acid in a vacuum. It was noticed, however, that under these conditions successive crops of the vitriolic sulphate alone crystallised out in the pure state. In one or two cases only, it was found that after a few crops of the pure vitrolic sulphate had crystallised out and the mother-liquor had become sufficiently rich in the sulphonium compound, the double salts began to put in an appearance. On using the metallic sulphates and the organic sulphate in the ratio of 1:2, the desired results were most strikingly secured. The double salts began to crystallise from the very beginning and in no case was any previous separation of the pure metallic sulphate observed. This peculiar behaviour was noticed even in the cases of manganese and magnesium compounds, where the metallic sulpates and the organic sulphate exist in the ratio of 2:1.

During crystallisation the mother-liquor assumed a thick syrupy state. The crystals of the double sulphates were drained free from the mother-liquor and dried by pressing between folds of a filter paper and analysed. The double salts are deliquescent and consequently unnecessary exposure to the atmosphere has to be carefully avoided.

In the preparation of nickel trimethyl sulphonium sulphate the proportion of the components used above and the procedure adopted were also the same.

Successive crops of the same preparation were collected in each case and found on analysis to give identical results.

Ferrous triethyl sulphonium sulphate.

It crystallised in long, white needles from solution, which was coloured red owing to slight decomposition. The crystals too decomposed in a day or two giving out ethyl sulphide. (Found : Fe, 8·35; C, 20·7₁*; H, 7·53 ; SO_4, 28·45. $FeSO_4,[(C_2H_5)_3S]_2$ SO_4, $10H_2O$ requires Fe, 8·38 ; C, 21·61; H, 7·56; SO_4, 28·83 per cent.).

Zinc triethyl sulphonium sulphate.

The double salt was obtained in white needle-shaped crystals. It is fairly stable in a dry atmosphere. (Found : Zn, 9·68 ; SO_4, 29·19. $ZnSO_4,|(C_2H_5)_3S]_2SO_4$, $10H_2O$ requires Zn, 9·67 ; SO_4, 28·42 per cent.).

Nickel triethyl sulphonium sulphate crystallised in long, greenish needles which are fairly stable. (Found : Ni, 8·71 ; SO_4, 29·01. $NiSO_4$, $[(C_2H_5)_3S]_2SO_4$, $10H_2O$ requires Ni, 8·77 ; SO_4, 28·70 per cent.).

Cobalt triethyl sulphonium sulphate.

The crystals obtained were coloured pink. (Found : Co, 8·86 ; SO_4, 29·32 ; $CoSO_4[(C_2H_5)_3S]_2SO_4$, $10H_2O$ requires Co, 8·80 ; SO_4, 28·69 per cent.),

Cadmium triethyl sulphonium sulphate.

The substance was obtained in white needle-shaped crystals. (Found : Cd, 15·39 ; SO_4, 27·68. $CdSO_4[(C_2H_5)_3S]_2SO_4$, $10H_2O$ requires Cd, 15·56 ; SO_4, 26·57 per cent.).

Magnesium triethyl sulphonium sulphate.

It crystallised in long white needles. (Found : Mg, 6·37 ; SO_4, 37·40 ; C, 17·36*; H, 6·74. $2MgSO_4,[(C_2H_6)_3S]_2SO_4$, $11H_2O$ requires Mg, 6·26 ; SO_4, 37·27 ; C, 18·63 ; H, 6·79 per cent.).

---

* Owing to the volatile nature of ethyl sulphide and sudden decomposition of the double sulphates during combustion, traces of the former escape un-oxidised, hence the carbon often comes out slightly low.

Manganese triethyl sulphonium sulphate.

The double salt was obtained in the shape of slightly pink-coloured crystals. (Found: Mn, 13·00 ; SO₄, 35·01. $2MnSO_4$, $[(C_2H_5)_3S]$, SO_4, $11H_2O$ requires Mn, 13·16 ; SO₄, 34·53 per cent.).

Nickel trimethyl sulphonium sulphate.

The double salt was obtained as green crystals. (Found: Ni, 15·62 ; SO₄, 37·74. $2NiSO_4[(CH_3)_3S]_2SO_4$, $11H_2O$ requires Ni, 15·48 ; SO₄, 38·02 per cent.).

The Compound of Triethyl Sulphonium Sulphate and Copper Sulphate.

The behaviour of copper sulphate with triethyl sulphonium sulphate was also studied. The sulphate solutions were mixed in the usual proportion and allowed to crystallise. After many days the blue solution assumed a very thick syrupy state from which after a further lapse of several days, bluish white, fine, silky needles began to separate out. The crystallisation was very slow and it was found extremely difficult to completely free the crystals from the adhering mother-liquor. Since sufficient amount could not be collected for analysis the composition was not determined. The small amount collected was very moist. On being preserved in a desiccator for a few days, it turned green. The blue compound could, however, be reproduced on exposure of the green compound to the moist atmosphere. A portion of the substance was held in a non-luminous flame on a platinum spatula and it was found to burn giving out a distinct smell of ethyl sulphide. This test suggests the formation of a true compound of triethyl sulphonium sulphate and copper sulphate.

Further investigation is in progress especially in the direction of the effect of substitution of ethyl by one or more of alkyl radicles like methyl, propyl, butyl, etc., on the composition of the resulting double salts.

In conclusion we beg to express our sincere thanks to Mr. Kshitish Chandra Bose-Ráy for his ungrudging help in conducting some of the experimental work in connection with the investigation.

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Action of Urea upon Thiosemicarbazides: Simultaneous Formation of Thiol-keto-triazolees, Amino-keto-thiodiazoles, Endoxytriazole and Amino-thiol-triazoles.

By Praphulla Chandra Guha and Pratul Chandra Sen.

1:4-Disubstituted thiosemicarbazides exist in two isomeric forms and their structure has been a subject of controversy between Busch and Marckwald. Marckwald (*Ber.*, 1892, **25**, 3098) and Dixon (*J. Chem. Soc.*, 1892, **81**, 1012) explain this phenomenon on stereo chemical grounds and Busch (*Ber.*, 1901, **34**, 320) explains it as being due to structural isomerides of the type $H_2N—NR—CS—NHR$ and $NHR \cdot NH \cdot CS \cdot NHR$. No such isomerism is known to exist among 4-monosubstituted thiosemicarbazides; still it cannot be said that there is no possiblity of the *syn-anti* isomerism of Marckwald with them, whilst Busch's position isomerism is out of the question.

$$H_2N—N \qquad\qquad H_2N—N$$
$$\|\qquad\qquad\qquad\qquad \|$$
$$HS—C—NHR \qquad RHN—C—SH$$
$$(syn) \qquad\qquad\qquad (anti)$$
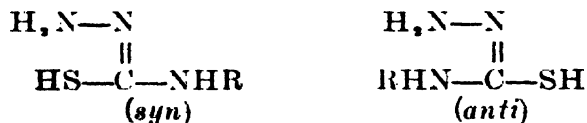
The present investigation was undertaken with the object of elucidating the nature of 4-mono-substituted thiosemicarbazides by observing their reaction with carbamide. Four different compounds are simultaneously formed in the reaction and their formation can be explained on the assumption that the thiosemicarbazides react both in the *syn-* and the *anti-*forms. The formation of 1-phenyl-2-keto-5-thiol-2:3-dihydro-1:3:4-triazole from 4-phenylthiosemi- carbazide may be explained by assuming the thiosemicarbazide to react in its *anti-*form, thus:

$$\begin{array}{ccc}
NH_2 & & NH \cdot N \\
| & H_2N—N & | \quad \| \\
CO + & \| & \xrightarrow{-2NH_3} \quad OC \quad C \cdot SH \qquad (\text{Type I}). \\
| & PhNH \cdot C \cdot SH & \vee \\
NH_2 & & NPh
\end{array}$$
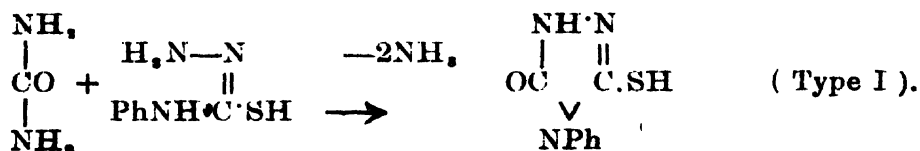
Such keto-thiol-triazoles were prepared by Freund and Schandei (*Ber.*, 1896, **29**, 2506), Arndt, Milde and Tschepscher (*Ber.*, 1922, **55**, 341) and by Fromm and Nehring (*Ber.*, 1923, **56**, 1370).

The formation of 2-keto-5-phenylamino-2:3-dihydro-1:3:4 thiodiazole necessitates the assumption of the *syn*-form :

$$
\begin{array}{cc}
\text{NH}_2 & \text{H}_2\text{N}\!-\!\text{N} \\
| & \quad\; \| \\
\text{CO} \; + & \\
| & \text{HS·C·NHPh} \\
\text{NH}_2 &
\end{array}
\xrightarrow[\longrightarrow]{-2\text{NH}_3}
\begin{array}{c}
\text{NH·N} \\
| \quad\;\; \| \\
\text{OC} \quad \text{C·NHPh} \\
\vee \\
\text{S}
\end{array}
\quad (\text{ Type IV })
$$
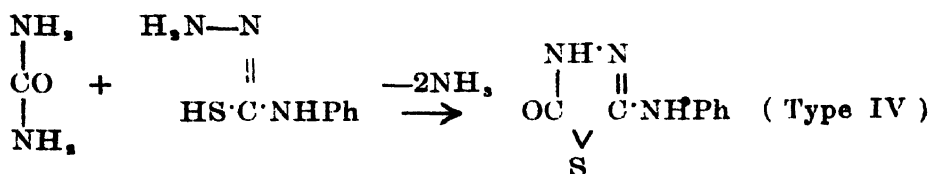
Similar keto-amino-thiodiazoles were prepared by Busch (*Ber.*, 1901, **34**, 320, **2328**; 1902, **35**,973; 1904, **37**, 2333; 1909, **42**, 4763; 1911, **44**, 561, 1580) and by Nirdlinger and Acree (*J. Amer. Chem. Soc.*, 1922, **44**, 224).

The compound formed at an intermediate stage during the formation of 2:5-endoxy-1:3:4-triazole may owe its formation to the *anti*-form of the thiosemicarbazide, thus :

$$
\begin{array}{cc}
\text{NH}_2 & \text{H}_2\text{N}\!-\!\text{N} \\
| & \quad\; \| \\
\text{CO} & +\text{PhNH·C·SH} \\
| & \\
\text{NH}_2 &
\end{array}
\longrightarrow
\text{PhNH}_2 + \text{NH}_3 +
\begin{array}{c}
\text{NH·N} \\
| \quad\;\; \| \\
\text{OC} \quad \text{C·SH} \\
\vee \\
\text{NH}
\end{array}
$$
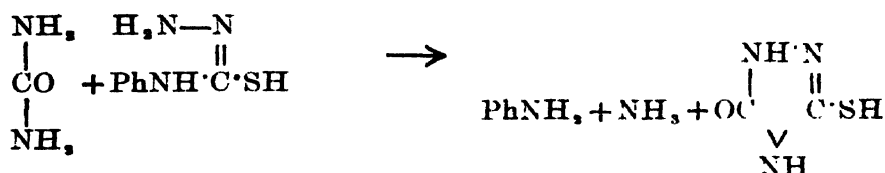
When this loses a molecule of sulphuretted hydrogen, the oxygen atom forms a bridge between the 2:5-carbon atoms so as to yield the endoxytriazole :

$$
\begin{array}{c}
\text{NH·N} \\
| \quad\;\; \| \\
\text{OC} \quad \text{C·SH} \\
\vee \\
\text{NH}
\end{array}
\longrightarrow
\begin{array}{c}
\text{N}\!-\!\text{N} \\
\| \quad\; \| \\
\text{HO·C} \quad \text{C·SH} \\
\vee \\
\text{NH}
\end{array}
\xrightarrow{-\text{H}_2\text{S}}
\begin{array}{c}
\text{N}\!-\!\text{N} \\
\| \quad\; \| \\
\text{C·O·C} \\
\vee \\
\text{NH}
\end{array}
\quad (\text{ Type III })
$$
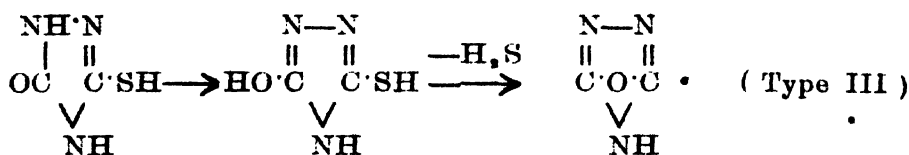
Though Marckwald, Busch and others prepared derivatives of endoxy-, endothio- and endoimino-triazoles*, the parent endoxytriazole has been prepared for the first time by the present authors.

Besides the three compounds mentioned above there is obtained 1-phenyl-2-phenylamino-5-thiol-1:3:4-triazole, for the formation of which urea is not required : one molecule of the thiosemicarbazide in the *syn*-form reacts with another in the *anti*-form with the

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* Schneider, *J. pr. Chem.*, 1890, **67**, 263 ; Marckwald, *Ber.*, 1892, **25**, 3113; 1896, **29**, 2923 ; Busch, *loc. cit* ; Nirdlinger and Acree, *loc. cit.*

splitting off of one molecule of sulphuretted hydrogen and one molecule of hydrazine, thus :

$$
\begin{array}{ccc}
\text{N·NH}_2 & \text{H}_2\text{N—N} & \text{N—N} \\
\|\ & \| & \|\ \ \| \\
\text{PhNH·C·SH} + \text{PhNH·C·SH} = \text{H}_2\text{S} + \text{NH}_2\text{·NH}_2 + \text{PhNH·C} \quad \text{C·SH} \\
& & \vee \\
& & \text{NPh} \\
& & (\text{Type II})
\end{array}
$$
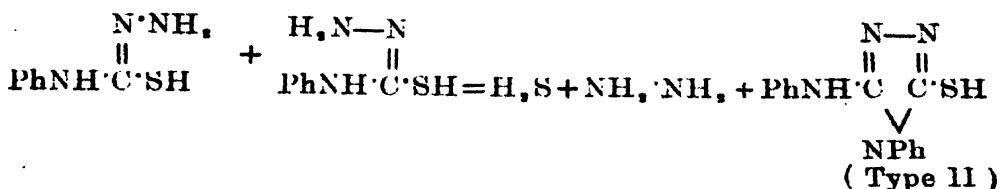
These four types of compounds have been obtained also from 4-tolyl- and 4-xylyl-thiosemicarbazides.

Urea reacts with thiosemicarbazide to give only two compounds, *viz.*, dihydroketo-thioltriazole and endoxytriazole, thus :

$$
\begin{array}{ccccc}
\text{NH}_2 & \text{H}_2\text{N—N} & & \text{NH·N} & \text{N—N} \\
| & \| & -2\text{NH}_3 & | \quad \| & \| \quad \| \\
\text{OC—NH}_2 & \text{H}_2\text{N·C·SH} \longrightarrow & & \text{OC} \quad \text{C·SH} \quad \xrightarrow{-\text{H}_2\text{S}} & \text{C·O·C} \\
& & & \vee & \vee \\
& & & \text{NH} & \text{NH}
\end{array}
$$
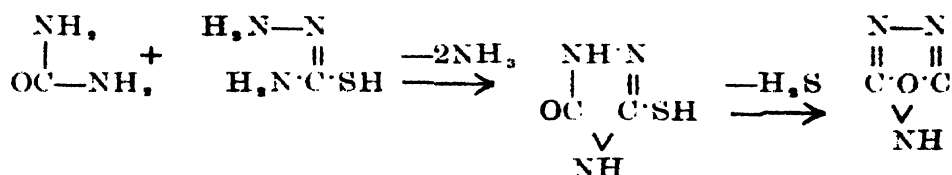
Seeing that the endoxy compound is invariably formed in the above reactions, it was naturally expected that the action of urea upon semicarbazide would yield this substance. In fact, it is formed, in good yield, when urea acts upon semicarbazide, to the exclusion of other compounds. Evidently, the reaction proceeds thus :

$$
\begin{array}{ccccc}
\text{H}_2\text{N} & \text{H}_2\text{N—NH} & & \text{NH·NH} & \text{N—N} \\
| & | & -2\text{NH}_3 & | \quad | & \| \quad \| \\
\text{CO} + & \text{CO} & \longrightarrow & \text{OC} \quad \text{CO} \quad \xrightarrow{-\text{H}_2\text{O}} & \text{C·O·C} \\
| & | & & \vee & \vee \\
\text{H}_2\text{N} & \text{NH}_2 & & \text{NH} & \text{NH}
\end{array}
$$
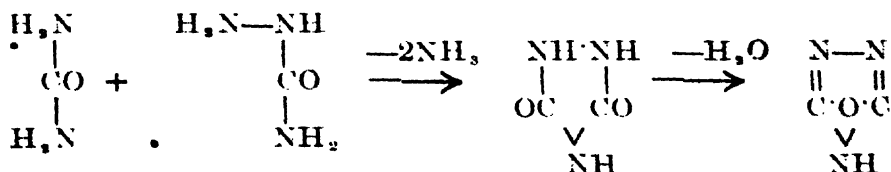
EXPERIMENTAL.

Four substances are produced simultaneously in the reaction between urea and a 4-R-thiosemicarbazide. These substances, the isolation of which depends on their respective solubilities are therefore taken in the following order : Type I, readily soluble in water; Type II, soluble in alkaline solution; Type III, soluble in boiling water; Type IV, insoluble in water and in alkaline solution.

Urea and 4-Phenylthiosemicarbazide.—4-Phenylthiosemicarbazide (10 g.) and freshly dried urea (8·5 g.) were thoroughly mixed and heated in an oil-bath at 130-135° during five to six hours. The mass began to melt at 120° and at 130° ammonia and sulphuretted

hydrogen were profusely evolved. After about one hour the reaction mixture assumed a brownish appearance which gradually disappeared as the heating was prolonged. After five hours' heating evolution of sulphuretted hydrogen came to an end, but there was still a slight liberation of ammonia. The reaction mixture was then poured into warm water (200 c.c.) and the pasty mass thus obtained was thoroughly triturated in a mortar; on being allowed to stand for some time in contact with water it solidified. The mixture was then filtered.

1-Phenyl-2-keto-5-thiol-2 : 3-dihydro-1 : 3 : 4-triazole.—(Type I).

Iodine dissolved in potassium iodide solution was added to the aqueous extract in slight excess when a voluminous precipitate was obtained. The precipitate was washed free from iodine with potassium iodide solution, and water, and was then heated under reflux with tin and hydrochloric acid for about an hour when the yellow mass gradually went into solution. It was filtered hot and on cooling gave a white crystalline mass which was crystallised from a large quantity of water, m.p. 197°. Arndt, Milde and Tschenscher (*loc. cit.*) give m.p. 196-197° ; yield 0·8 g. It is soluble in alkali, gives insoluble lead and mercury mercaptides, and is oxidised to a yellow disulphide on exposure to the air. (Found : N, 20·32. $C_8H_7ON_3S$, H_2O requires N, 19·91 per cent.).

The Disulphide.—The yellow precipitate obtained by the addition of iodine to the aqueous extract was further purified by crystallisation from dilute alcohol, m.p. 290°. Arndt (*loc. cit.*) gives m.p. 286°. (Found : N, 21·23. $C_{16}H_{11}O_2N_6S_2$ requires N, 21·98 per cent.).

The Dimethyl Derivative.—The phenyl triazole (0·5 g.) was dissolved in dilute potassium hydroxide solution and shaken vigorously with methyl iodide (2 c.c.) for a few minutes when a white crystalline precipitate separated : it crystallised from water in fine soft needles, m.p. 110.° (Found : N, 18·88. $C_{10}H_{11}ON_3S$ requires N, 19·00 per cent.).

The solid insoluble product was thoroughly triturated in a mortar with normal sodium hydroxide solution when a portion was found to have gone into solution ; the mixture was filtered.

1-Phenyl-2-phenylamino-5-thiol-1 : 3 : 4-triazole.—(Type II.).

The filtrate was neutralised with dilute hydrochloric acid when a white amorphous precipitate was obtained. It was crystallised from

dilute acetone, m.p. 210°; yield 1·8 g. (Found: S, 12·27. $C_{14}H_{12}$ N_4S requires S, 11·94 per cent.). It gives an insoluble disulphide with iodine.

The *methyl derivative* was prepared by shaking the above substace (0·5 g.) in sodium hydroxide solution with methyl iodide (3 c.c.). It was crystallised from dilute alcohol; m.p. 209°. (Found: N, 19·23. $C_{15}H_{14}N_4S$ requires N, 19·86 per cent.).

The *benzyl* derivative was prepared by heating molecular quantities of the thiol compound and benzyl chloride in alcoholic sodium hydroxide solution (1 mol.) under reflux for about half an hour. After removing the alcohol, the residue was freed from sodium chloride by washing with boiling water. Finally, it was crystallised from dilute alcohol, m.p. 153-154°. Fromm *(Annalen, 433, 1)* gives m.p. 154°.

2:5-*Endoxy*-1:3:4-*triazole*.—(Type III).

The insoluble residue was boiled repeatedly with large quantities of water and filtered hot; the filtrate gave a beautiful white crystalline mass which was crystallised from a large quantity of water, m.p. 250°; it is insoluble in alkali and acetone ; yield 2 g. (Found: N, 50·82. C_2HON_3 requires N, 50·60 per cent.).

N-*Acetyl-endoxytriazole*.—The above endoxy compound (1·5 g.) was boiled under reflux with acetic anhydride (5 c.c.) for three hours and the reaction mixture poured into water: a white precipitate was obtained which was crystallised twice from water; m.p. 242°. (Found: N, 33·55. $C_4H_3O_2N_3$ requires N, 33·60 per cent.).

2-*Keto*-5-*phenylamino*-2:3-*dihydro*-1:3:4-*thiodiazole*.—(Type IV)

The residue insoluble in water and aqueous alkali, after crystallisation from dilute acetone, had m.p. 246° ; yield 0·5 g. (Found: N, 21·3. $C_8H_7ON_3S$ requires N, 21·76 per cent.).

Urea and p-*Tolylthiosemicarbazide*.

An intimate mixture of 4-*p*-tolylthiosemicarbazide (9 g.) and freshly dried urea (7·5 g.) was heated in an oil-bath at 130-135° for about six hours when ammonia and sulphuretted hydrogen were profusely evolved. By following the process of extraction gone through in the previous case, an aqueous extract and a solid were obtained.

Isolation of the Disulphide of 1-*Tolyl-2-keto-5-thiol-2৹3-di-hydro-*1:3:4-*triazole.*—(Type I).

The aqueous extract gave with iodine solution a voluminous precipitate which was washed with potassium iodide solution and water and was further purified by precipitation from an alcoholic solution by the addition of water, m.p. 175°; yield 1·3 g. (Found: N, 20·55. $C_{18}H_{16}O_2N_6S_2$ requires N, 20·38 per cent.).

Dimethyl derivative.—The disulphide (1 g.) was reduced with tin and hydrochloric acid by heating under reflux for about an hour. The disulphide gradually went into solution and on diluting this, a white precipitate was obtained. The precipitate after being washed several times with water was quickly dissolved in alkali and shaken well with methyl iodide (2·5 c.c.). After some time a white crystalline mass separated which was purified by crystallisation from water, m.p. 142°. (Found: N, 17·92. $C_{11}H_{13}ON_3S$ requires N, 17·87 per cent.).

The solid, left after the product of reaction was digested with water, was treated with alkali when a portion went into solution.

1-*Tolyl-2-tolylamino-5-thiol-*1:3:4-*triazole*—(Type II).

The alkaline solution gave a white amorphous precipitate on acidification with hydrochloric acid, which was crystallised from dilute acetone, m.p. 187°; yield 1·5 g. (Found: S, 10·85. $C_{16}H_{16}N_4S$ requires S, 10·81 per cent.). It gives a yellow disulphide with iodine.

Benzoyl derivative.—The above substance (0·6 g.) was dissolved in alkali and shaken with benzoyl chloride (3·5 c.c.). A faintly yellow precipitate separated; this was collected, washed with dilute alkali and water, and crystallised from acetone, m.p. 100°. (Found: S, 7·86. $C_{23}H_{20}ON_4S$ requires S, 8·0 per cent.).

Methyl derivative.—Methyl iodide (3 c.c.) was added to an alkali solution of the substance (0·6 g.) and the mixture was vigorously shaken when a crystalline precipitate separated: it was crystallised from water, m.p. 178°. (Found: N, 18·04. $C_{17}H_{18}N_4S$ requires N, 18·06 per cent.).

2:5-*Endoxy-*1:3:4-*triazole.* —(Type III).

The residue was treated with a large quantity of boiling water; the filtrate gave crystals, m.p. 250°, in every respect identical with the substance obtained from 4-phenylthiosemicarbazide.

2-Keto-5-tolylamino-2 : 3-dihydro-1 : 3 : 4-thiodiazole.—(Type IV).

The solid which remained after treatment with boiling water was crystallised from alcohol (90 per cent.), m.p. 227° (Found: N, 20.13. $C_9H_9ON_3S$ requires N, 20.29 per cent.).

Urea and Xylyl-thiosemicarbazide.

A mixture of 4-xylyl-thiosemicarbazide (10 g.) and freshly dried urea (7.5 g.) was heated at 130-140° for about six hours during which ammonia and sulphuretted hydrogen were profusely evolved. The same process as before was followed for separating the four products of this reaction.

1-Xylyl-2-keto-5-thiol-2 : 3-dihydro-1 : 3 : 4-triazole.—(Type I).

As in the case of the phenyl and tolyl compounds, a yellow insoluble disulphide was obtained from the aqueous extract. This was reduced with tin and hydrochloric acid : on dilution with water the solution gave a white crystalline precipitate. It was thoroughly washed with water, crystallised from dilute hydrochloric acid and dried in a vacuum desiccator, m.p. 195° ; yield 0.6 g. (Found : N, 19.32. $C_{10}H_{11}ON_3S$ requires N, 19.00 per cent.).

The Disulphide.—The crude disulphide obtained by the addition of iodine to the aqueous extract, was purified by dissolving in acetone and precipitating with water, m.p. 240°. (Found : N, 19.17. $C_{20}H_{20}O_2N_6S_2$ requires N, 19.09 per cent.).

The solid, insoluble in water, was treated with dilute alkali when a portion went into solution.

1-Xylyl-2-xylylamino-5-thiol-1 : 3 : 4-triazole.—(Type II).

The alkaline extract on acidification with dilute hydrochloric acid gave a white amorphous precipitate which, after crystallisation from acetone, had m.p. 200°, yield 0.8 g. (Found : S, 9.39. $C_{18}H_{20}N_4S$ requires S, 9.87 per cent.).

2 : 5-Endoxy-1 : 3 : 4-triazole.—(Type III).

The residue was boiled several times with large quantities of water. The aqueous solution yielded a substance, m.p. 250° identical with the endoxytriazole already obtained.

2-Keto-5-xylylamino-5-thiol-1 : 3 : 4-thiodiazole.—(Type IV).

The insoluble residue was crystallised from dilute acetone, m.p. 218-219°. (Found : N, 18.97 . $C_{10}H_{11}ON_3S$ requires N, 19.00 per cent.).

Urea and Thiosemicarbazide.

A mixture of thiosemicarbazide (6 g.) and freshly 'dried' urea (10 g.) was heated for six hours at 125-130° during which ammonia and sulphuretted hydrogen were evolved. The molten mass was then well ground with water in a mortar and the solid residue was found to be insoluble in alkali. It was crystallised from a large quantity of water when it melted at 250°. It was found to be identical with the endoxytriazole already obtained.

Isolation of Keto-thioltriazole Disulphide.

The cold aqueous extract was treated gradually with iodine solution when a yellow precipitate was obtained which dissolved again on shaking. After iodine was added in excess, the solution was evaporated to half its bulk and cooled when a small quantity of a white crystalline precipitate came out, m.p. 246°. As the yield of the disulphide was very poor, the parent substance (thiourazole) could not be prepared. Arndt, Milde and Tschenscher (*loc. cit.*) give the m.p. 246° for the disulphide. (Found: N, 36·93. $C_4H_4O_2N_6S_2$ requires N, 36·20 per cent.).

Action of Urea upon Semicarbazide.

A mixture of semicarbazide (5 g.) and freshly dried urea (10 g.) was heated at 140° for about six hours. By following the process indicated above, endoxytriazole melting at 250° was obtained ; yield 4 g. Neither the aqueous nor the alkaline extract gave any other compound. Evidently, the reaction proceeds in this case only in one direction.

The action of thiourea upon semicarbazides and thiosemicarbazides is being studied and will form the subject of a subsequent communication.

Our thanks are due to Sir P. C. Rây and Dr. J. C. Ghosh for the kind interest they have taken during the progress of this investigation.

Formation of Heterocyclic Compounds. Part II.

By Hemendra Kumar Sen and Umaprosanna Bose.

In a system containing a conjugated double bond of the type $O=C-C=CR$, the ethylenic linkage is generally found to be more active than the carbonyl (Harries and Lellmann, *Ber.*, 1897, **30**, 230, 2726; Harries and Jablonski, *Ber.*, 1898, **31**, 1371 ; Vorlander, *Ber.*, 1894, **27**, 2053 ; *Annalen*, 1897, **294**, 273; Lapworth, *J. Chem. Soc.*, 1904, **85**, 1214 ; Knoevenagel, *Ber.*, 1904, **37**, 4464 ; Sen Gupta, *J. Chem. Soc.*, 1915, **107**, 1347). To ascertain the position of the ethylenic bond is thus a matter of considerable importance in determining the constitution of synthetic products derived from such systems, three types which may be cited for our present purpose :

$$O=C-C=C.R \qquad O-C=C.OH \qquad O=C-C=C(OH).$$
$$\text{I.} \qquad\qquad\qquad \text{II.} \qquad\qquad\qquad \text{III.}$$
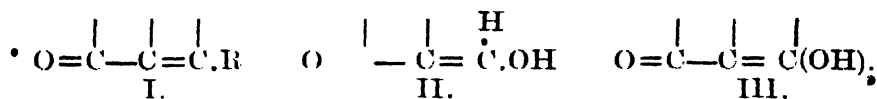
These represent benzylidene acetone, hydroxymethylene ketone and acetyl acetone respectively. It is usually found that in the first case the ethylenic linkage is more reactive than the carbonyl. Thus in the reduction of unsaturated ketones of the general formula, $R_2C=CH\cdot CO\cdot R$, the ethylenic linkage is the one which is primarily attacked whilst the carbonyl group is affected only secondarily (*cf.* Harries, *loc. cit.*). The same is true of the addition of hydroxylamine, ammonia (Koehl and Dinter, *Ber.*, 1903, **36**, 172), hydrogen cyanide, etc. (*cf.* Lapworth, *loc. cit.*). Vorlander (*Ber.*, 1894, **27**, 2053) has shown that the ethylenic linkage alone is involved in the reaction between sodium malonic ester and derivatives of cinnamic acid, $C_6H_5\cdot CH=CH\cdot CO\cdot X$, where X represents any group. There are, however, examples which do not support this view, such as the reduction of cinnamyl formic acid to phenyl-hydroxyisocrotonic acid (Erlenmeyer, jun., *Ber.*, 1903, **36**, 2529 ; 1904, **37**, 1318), and the addition of hydrogen cyanide and magnesium methyl iodide to the carbonyl group of cinnamic aldehyde (Kohler,

Like most chemical hypotheses, therefore, the principle that in a
conjugated double bonded system the ethylenic linkage is more
reactive, requires to be critically examined before the few exceptions
like those mentioned above could be regarded as arguments against it.

In a system of the second type, as shown by one of us (Sen
Gupta, *loc. cit.*), the ethylenic linkage is far more reactive than the
carbonyl. Thus the condensation of hydroxymethylene *cyclohe-
xanone* and cyanacetamide leads to the formation of quinoline and
not *isoquinoline* derivatives, as proved definitely by the isolation of
pure quinoline by zinc dust distillation.

$$\longrightarrow \text{Quinoline.}$$
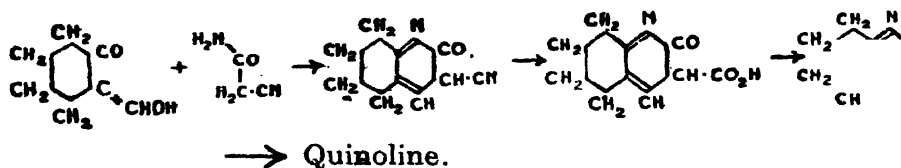
Arguments may be put forward against this conception on the ground
that hydroxymethylene ketones are also capable of existing in the
keto-aldehyde phase and that the formyl group which is thus pro-
duced in the molecule, being more reactive than the ketone, gives
rise to the same set of products as demanded by the superior re-
activity of the ethylenic linkage. But since the identical quino-
line derivative was obtained by condensing either hydroxymethy-
lene *cyclo*hexanone or its acetate,

$$CH_2 < \begin{matrix} CH_2-CH_2 \\ CH_2-\!\!-\!\!-C \end{matrix} = CH \cdot OCO \cdot CH_3 > CO$$
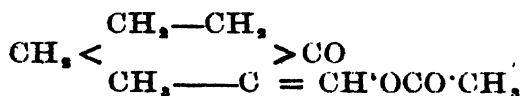
with cyanacetamide, the main theorem that the ethylenic linkage
in a conjugated system is more reactive than the ketonic group,
is not affected thereby.

Quite different is the case with 1:3-carbonyl compounds, for,
like the unsaturated type (I) or hydroxymethylene ketones (type II),
they do not possess any ethylenic bond in themselves as represent-
ed in the ordinary structural formulae. It is only when they
tautomerise to their enolic modifications, that conjugated double
bonds of the same type as in (I) and (II) are set up. The question
now arises whether in reacting with such compounds, the ethylenic
linkage formed is responsible for the initial condensation or the

carbonyl group, remaining as such, becomes the centre of reaction ?
A. suitable reagent to test this point is found in cyanacetamide
where the methylene group is readily reactive. The point here is
whether the addition of the methylene group takes place at the
double bond, or it reacts with the carbonyl group with the elimi-
nation of water?

In the literature which has special reference to the chemistry
and condensation of β-diketones (or β-ketonic esters), the work of
Moir (*J. Chem. Soc.*, 1902, **81**, 100) and that of Simonsen (*J. Chem.
Soc.*, 1908, **93**, 1022) are noteworthy. The former is significant
from the fact that Moir thoroughly investigated the compound ob-
tained by condensing acetyl acetone with ethyl cyanacetate in the
presence of an excess of ammonia, and claims to have established
the mechanism of all such reactions. According to him, the first
part of the reaction involves the formation of cyanacetamide and
aetyl acetonamine which then react with each other to give the
closed ring system as shown below :—

$$CH_3 \cdot CO \quad \quad CH_2 \cdot CN \quad CH_3 \cdot CO \quad \quad CH_2 \cdot CN$$
$$| \quad \quad \quad | \quad \quad \quad | \quad \quad \quad |$$
$$CH + 2NH_3 + \quad CO \quad \rightarrow \quad CH \quad + \quad CO + H_2O + C_2H_5OH$$
$$\| \quad \quad \quad \quad | \quad \quad \quad \| \quad \quad \quad |$$
$$CH_3 \cdot C \cdot OH \quad \quad OC_2H_5 \quad CH_3 \cdot C \cdot NH_2 \quad \quad NH_2$$

$$CH_3 \cdot C = C \cdot CN$$
$$| \quad \quad |$$
$$CH \; CO \quad + NH_3 + H_2O$$
$$\| \quad \quad |$$
$$CH_3 \cdot C - NH$$

(IV.)
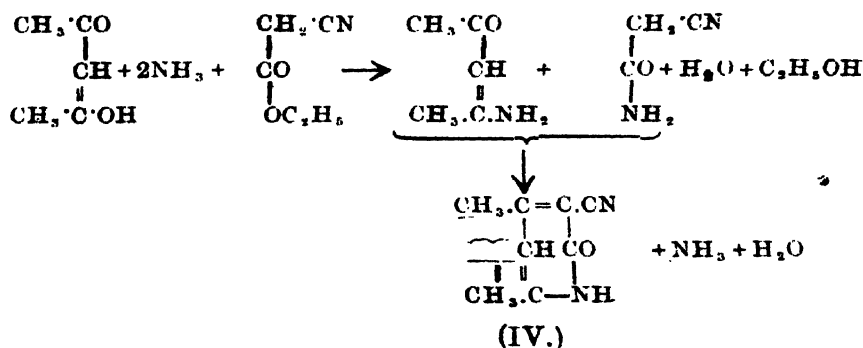
Moir preferred this mechanism owing to the reason that on heating
acetylacetonamine with cyanacetmethylamide, the sole product
of the reaction was the *N*-methyl derivative of (IV). But the re-
action is quite as readily explained by applying the general theorem
upheld in this investigation :

$$CH_2 \cdot CO \quad HN \cdot CH_3 \quad CH_2CO \quad HN \cdot CH_3 \quad CH_3 \cdot C(OH)HN \cdot CH_3 \quad CH_3 \cdot C - N \cdot CH_3$$
$$| \quad \quad | \quad \quad | \quad \quad | \quad \quad | \quad \quad | \quad \quad \| \quad \quad |$$
$$CH + CO \rightarrow \quad CH_2 \quad CO \rightarrow \quad CH \quad CO \rightarrow \quad CH \; CO$$
$$\| \quad \quad \quad | \quad \quad \quad | \quad \quad \quad | \quad \quad \quad | \quad \quad \quad |$$
$$CH_3 \cdot C \cdot NH_2 \quad CH_2CN \quad CH_3 \cdot C - CH \cdot CN \quad CH_3 C === C \cdot CN \quad CH_3 C = C \cdot CN$$
$$\quad \quad \quad \quad NH_2$$
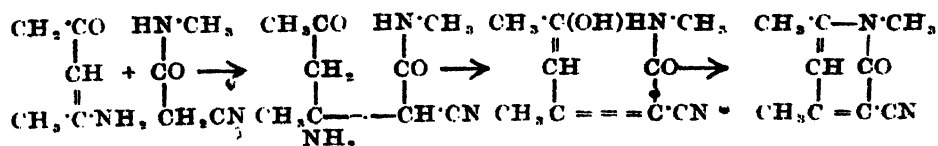
If Moir's explanation were general, the condensation of hydro-
xymethylene *cyclo*hexanone with cyanacetamide should yield an

*iso*quinoline derivative, whereas this is not the case. Moreover, identical products are obtained whether one condenses hydroxyme-thylene *cyclo*hexanone with cyanacetic ester in alcoholic ammonia, or the amide of hydroxymethylene *cyclo*hexanone with ethyl cyan-acetate in presence of diethylamine or piperidine (Sen Gupta, *loc. cit.*, p. 1355).

The next point to be considered is, Which of the carbonyl groups enolises in the case of a β-diketone? If symmetrical groupings be present in the molecule such as in acetyl acetone, the question does not arise. The case of unsymmetrical β-diketones, such as benzoyl acetone, has been thoroughly investigated by Bardhan (Thesis for the D.Sc. Degree of the University of Calcutta. 1924), who finds that the negative nature of the group favours enolisation which determines the more reactive centre of condensation. Whether the presence of one of the ketonic groups in a cyclic compound influences its activity was necessarily considered to be of importance in establishing the general character of Bardhan's hypothesis. As already mentioned (*loc. cit.*) if the enolisation is not exclusively limited to one particular ketonic group, there would be isomeric condensation products possible. Accordingly acetyl *cyclo*hexanones were taken and the course of their reaction with cyanacetamide was studied in the presence of Knoevenagel's as well as Michael's reagent, with a view further to examine the directive influence of these condensing agents.

The experimental evidence so far shows that acetyl *cyclo*hexanone and cyanacetamide condense to give rise to a mixture of quinoline and *iso*quinoline derivatives, thus indicating that the reduced cyclic residue has no special directive influence on the enolisation. But that the enolisation of a carbonyl group is at the bottom of such reactions is proved by a significant negative result obtained in the course of this investigation on attempting to condense 2-acetyl-2-methyl-*cyclo*hexanone-1 with cyanacetamide in presence of piperidine. No condensation product could be readily obtained, but on keeping the reaction mixture overnight, a very small quantity of a substance was isolated which on methylation melted at a temperature almost identical with the melting point of the compound obtained by methylating the condensation product of acetyl-*cyclo*hexanone and cyanacetamide. There was no doubt that in the experiment recorded acetyl*cyclo*hexanone was methylated, as by heating the me-thylated acetyl-*cyclo*hexanone with potash, *o*-methyl-*cyclo*hexanone was obtained (*vide* Experimental part). The removal, therefore, of

the labile hydrogen atom necessary for the enolisation of the ketonic group had rendered such condensations impossible or at least very difficult (*cf.* Rogerson and Thorpe, *J. Chem. Soc.*, 1905, **87**, 1685; Haworth, *J. Chem. Soc.*, 1909, **95**, 480). The small quantity of product that separated could have thus been possible from any the least quantity of acetyl-*cyclo*hexanone escaping methylation. Of far reaching consequence is the interpretation of this negative result, as it further disproves the ordinarily accepted mechanism of Knoevenagel's reaction (*cf.* Ingold, *J. Chem. Soc.*, 1921, **119**, 329).

It is next of importance to decide as to which of the two groups, methylene (CH₂) or the amido of cyanacetamide takes the precedence in the addition to the enolised double bond. As the electropositive character of the admidic hydrogen is far less than that of the methylene hydrogen of cyanacetamide, it is highly improbable that the former should add on to the double bond in preference to the latter. Besides the production of quinoline derivatives in the condensation of hydroxymethylene ketones with cyanacetamide (*J. Chem. Soc.*, 1915, **107**, 1347) definitely establishes the greater affinity of the methylene group for the double bond in a conjugated system. This fact goes directly against Moir's hypothesis. It should be mentioned in this connection that Moir's preference to his own mechanism of reaction was greatly actuated by his supposed difficulty of eliminating a molecule of water for the closure of ring when alkyl substituted amides were taken. That this difficulty is imaginary was shown by our method of representing such reaction (*loc. cit.*). He had not also thought of the other contingency, namely, substitution of a methylene hydrogen atom of cyanacetamide by alkyl. This we have done and found that acetyl-*cyclo*hexanone and methyl-cyanacetamide, CN.CH(CH₃)CO.NH₂ yield the same product as the one from acetyl-*cyclo*hexanone and cyanacetamide itself, eliminating thus not two molecules of water, but one molecule of water and one molecule of methyl alcohol :
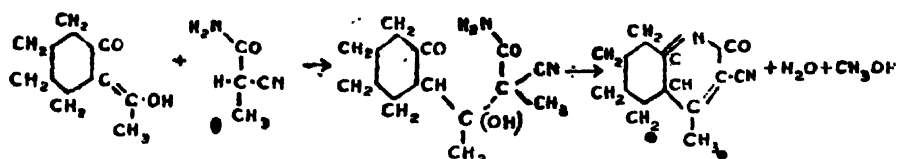
This again points to the correctness of our view that in a conjugated double bonded system, the ethylenic linkage is more

reactive than the carbonyl, particularly in respect to cyanacetamide and similar substances. Expressed otherwise, in β-diketones even the ketonic group acts through setting up of ethylenic linkage. It is in the light of these experiments that Moir's explanation of the mechanism of reaction between cyanacetamide and acetylacetone is discarded, as, according to him, there is no provision for the enolisation of the ketonic group before its reaction with the methylene group of cyanacetamide.

When acetyl *cyclo*hexanone is condensed with cyanacetamide in aqueous—alcoholic solution in the presence of piperidine, a product is obtained, which dissolves in alkali forming a colourless solution from which it is precipitated unchanged by the addition of acid. On hydrolysing the substance with fuming hydrochloric acid, the cyanogen group is eliminated. From the solubility or from any other property of the hydrolysed product, it is not possible to determine whether the condensation product is a mixture or a single substance.

The reasons which have led to the conclusion that the condensation product is a mixture of quinoline and *iso*quinoline derivatives are as follows.

(1) On hydrolysing the condensation product, the cyanogen group is split off. The product may be a mixture of
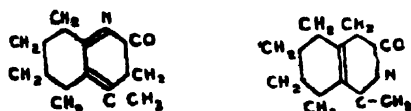
or one of these. The hydrolysed product (having the benzene ring fully reduced) yielded, on distillation with zinc dust in a current of hydrogen at a low red heat, a heavy liquid of quinoline like odour. On redistilling the mixture over heated litharge, a purer liquid of quinoline like smell and colour boiling at 239° was obtained. This gave a picrate having a melting point lower than that of γ-methyl quinoline or α-methyl*iso*quinoline. Similarly, a methiodide well crystallisable but of an indifferent melting point was obtained.

(2) The condensation product gave a methyl ether which, after fractional crystallisation, yielded different crops having different melting points but the same percentage composition. This is only possible if the mother substance be a mixture of two isomers.

(3) The hydrolysed products have no sharp melting points.

If now the condensation product obtained from acetylcyclohexanone and cyanacetamide be regarded as mixtures it is clear that by

fixing the enolising carbon atom one should get either a quinoline or an isoquinoline derivative. Accordingly ethyl *cyclo*hexanone carboxylate was taken as a suitable reagent for testing this view. The labile hydrogen in the carboxylate can only enolise the ketonic oxygen and as such the reaction with cyanacetamide whether in the presence of sodium ethoxide or piperidine, should be represented as below.
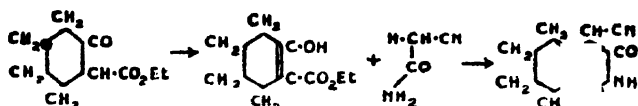
The product obtained in this way corresponds to the above composition and melted after crystallisation at 278-280°, shrinking only a few degrees earlier. This characteristic of sharp melting point is absent in similar products obtained from acetyl*cyclo*hexanone and cyanacetamide and leads one to regard it as a pure product and not a mixture. It would be important now to resolve this provisionally accepted *iso*quinoline derivative into simpler products and finally distil it with zinc dust to obtain *iso*quinoline itself. This will be undertaken as soon as time and opportunity permit.

EXPERIMENTAL.

Condensation of 2-Acetylcyclohexanone with Cyanacetamide.

2-Acetyl-*cyclo*hexanone was prepared according to Leser's method (*Bull. Soc. Chim.*, 1900, (iii), **23**, 370; *cf.* Borsche, *Annalen*, 1910, **377**, 70) and obtained as a colourless liquid boiling at 108-111° under 20 mm. pressure. The yield was about 32 per cent. of the weight of *cyclo*hexanone used.

Cyanacetamide (6 g.) was dissolved in water by warming, and 2-acetyl-*cyclo*hexanone (10 g.) added with just enough alcohol to effect the solution. About one c.c. of piperidine being added, the solution was then warmed up to 60° when after 3 or 4 minutes crystals began to separate. The flask was then kept for a while at a temperature of about 40°, when its contents set to a crystalline solid. The flask was loosely corked and left overnight at the room temperature. Next day the condensation product (about 11 g.) was collected. The mother-liquor, on evaporation, gave about 1·5 g. more of it.

The condensation product was moderately soluble in boiling glacial acetic acid from which it was btained in colourless prismatic needles, darkening at 280°, and beginning to decompose at about

290°. This compound was already described by one of us (Sen Gupta, *loc. cit.*), but no further work regarding its constitution was since taken in hand.

The same compound can be obtained by condensing 2-acetyl-*cyclo*hexanone with cyanacetamide in the presence of sodium ethoxide as follows.—Sodium (0·35 g.) was dissolved in absolute alcohol. An alcoholic solution of cyanacetamide (1·2 g.) was added to the sodium ethoxide solution. To the sodium salt of cyanacetamide thus precipitated, acetyl *cyclo*hexanone (2 g.) was gradually added with shaking. The sodium salt dissolved, and the solution, which assumed a deep yellow colour, was left overnight. Next morning the solution, after being diluted with water, was acidified with dilute hydrochloric acid when the condensation product (about 2 g.) was obtained. Crystallised from glacial acetic acid with the addition of a few drops of water, the product was obtained in colourless prismatic needles which begin to decompose above 290°. (Found: N, 14·98. $C_{11}H_{12}ON_2$ requires N, 14·89 per cent.).

These condensation products are insoluble in cold water, very sparingly soluble in boiling water or alcohol. They readily dissolve in alkali to a colourless solution from which they are reprecipitated unchanged by the addition of acid. Concentrated hydrochloric acid dissolves them ; from the acid solution they are precipitated on dilution with water. Ferric chloride imparts no colouration to their alcoholic solution.

Hydrolysis of the Condensation Product.—The condensation product (4 g.), obtained by using piperidine as the condensing agent, was heated with fuming hydrochloric acid (28 c. c.) in a sealed tube for four hours at 170°. A substance crystallised in the tube; this was washed carefully and recrystallised from a minimum quantity of water. It was found to be a hydrochloride : it forms colourless needles, sintering at 205° but melting completely at 252°. (Found: N, 6·84; Cl, 17·54. $C_{10}H_{13}ON, HCl$ requires N, 7·01; Cl, 17·79 per cent.).

The substance is soluble in water, reacts acid towards litmus, forms an insoluble silver chloride with silver nitrate solution, and readily decolourises aqueous permanganate. It is also soluble in alcohol to which ferric chloride imparts a deep red colouration. Concentrated hydrochloric acid dissolves it; from the solution it can be reprecipitated on dilution with water. The hydrochloride, when dissolved in boiling water and gradually neutralised with sodium carbonate, yields the hydroxybase which is obtained from alcohol in

colourless needles sintering at 225° and melting at 235°. The compound has no sharp melting point. (Found: N, 8·94. $C_{10}H_{13}ON$ requires N, 8·59 per cent.).

The hydroxybase is less soluble in water. Its aqueous solution is neutral to litmus. It is soluble in alcohol, concentrated hydrochloric acid and alkali? Ferric chloride imparts a deep red colouration to their alcoholic solution.

Reduction of the Hydroxybase.—The hydrolysed product (7 g.) was intimately mixed with zinc dust (50 g.) in an ordinary combustion tube with one of its ends drawn out and bent. The front part of the tube contained a length of about 12 cm. of zinc dust. The distillation was conducted at a low red heat in a current of hydrogen, when ammoniacal vapours began to escape. In course of half an hour about 1·5 g. of a dark yellowish liquid collected. The liquid thus obtained was mixed with litharge in a hard glass tube closed at one end. This was heated to dull redness in a combustion furnace when a reddish yellow liquid having the odour of quinoline distilled over, ammoniacal vapours escaping condensation at the same time. The liquid was dissolved in dilute hydrochloric acid, shaken up with ether to remove any non-basic impurities and reprecipitated by the addition of alkali. The ethereal extract of the base was dried over anhydrous sodium sulphate and distilled. A clear liquid, which soon turned yellow, was collected at about 239° which gave a picrate melting indifferently between 189° and 194° after crystallisation. Another crop of it was obtained from the mother-liquor which melted at 154°-155°, sintering and moistening a few degrees earlier. A methiodide was obtained which also melted indifferently between 174° and 176° and the mother-liquor yielded a product having a melting point of 136°-137°. [Found (for picrate, m.p. 189-94°): N, 14·78; (for picrate, m.p. 154-55°) N, 15·87. Methylquinoline or methyl *iso*quinoline picrate requires N, 15·05 per cent.].

Probably during zinc dust distillation or litharge oxidation the methyl group was partially eliminated yielding quinoline and *iso*quinoline. Quinoline or *iso*quinoline picrate requires N, 15·64 per cent. That both the methyl quinolines are simultaneously formed is proved from the fractional isolation of methyl ethers.

Methyl Ether.—The condensation product (2 g.) obtained from acetyl*cyclo*hexanone and cyanacetamide was dissolved in dilute alkali and treated with an excess of dimethyl sulphate. The solution, which became warm, was then gently heated to boiling, maintained alkaline and the precipitate formed collected. When crystallised

from water, the methyl ether had no sharp melting point. Repeated fractional crystallisation from water, however, gave a product which melts at 179°-180°. The mother-liquor yielded two crops, one melting at 175° and the other at 158°, but sintering a few degrees earlier. The mixed m.p. of the first crop melting at 179°-180° with that melting at 158° was 170°-173°. The crop melting at 179°-180° was recrystallised when an ether having m.p. 182°-183° was obtained [Found : N, 14·07 (first crop); N, 13·96 (second crop). $C_{13}H_{14}ON_2$ requires N, 13·87 per cent.]. The two methyl ethers are therefore identical in composition, though isomeric.

Condensation of 6-Methyl-2-acetyl-cyclohexanone and Cyanacetamide.

The acetyl compound was prepared in the usual way from o-methylcyclohexanone which yields about 20 per cent. of its weight of 6-methyl-2-acetyl-cyclohexanone as a colourless liquid boiling at 115-120°/25 mm.

The condensation was effected, as usual, by means of piperidine. The condensed product was somewhat more soluble in dilute alcohol than its previous analogue. The yield in this case was about 84 per cent. of the theory. It crystallises from dilute acetic acid in fine prismatic needles, darkening above 250° and finally melting with decomposition at 275°. (Found : N, 14·20. $C_{12}H_{14}ON_2$ requires N, 13·87 per cent.). The substance is soluble in boiling water; it dissolves in alkalis to a colourless solution from which it is partially precipitated unchanged by the addition of acid. No methyl ether was obtained by treating its alkaline solution with dimethyl sulphate.

On hydrolysis with fuming hydrochloric acid, a compound was obtained which was very soluble in concentrated acid. It was isolated by evaporating the acid solution to dryness and extracting the residue with boiling absolute alcohol. On cooling needle-like crystals separated out. Recrystallised from rectified spirit the substance melted at 242-243°. (Found : N, 8·15. $C_{11}H_{15}ON$ requires N, 7·91 per cent.).

The hydrolysed product is not appreciably soluble in water, and silver nitrate solution has no action on it. It possesses a sharp melting point and melts without decomposition. In this respect it differs from any of its other homologues.

Condensation of 5-Methyl-2-acetylcyclohexanone and Cyanacetamide.

The diketone was obtained as a colourless oil, b.p. 128-29°/19

mm. The yield was about 32 per cent. of the weight of m-methyl-cyclohexanone used.

The condensation product was prepared as usual. Crystallised from glacial acetic acid with the addition of a few drops of water, it was obtained in prismatic needles darkening above 260° and showing no sign of melting even at 280°. The yield in this case is almost theoretical. (Found: N, 13·92. $C_{12}H_{14}ON_2$ requires N, 13·87 per cent.).

The compound obtained by hydrolysing the condensation product with fuming hydrochloric acid crystallises from rectified spirit in long needles sintering at 195° and melting at 200-201°. (Found: N, 8·23. $C_{11}H_{13}ON$ requires N, 7·91 per cent.).

Condensation of 4-Methyl-2-acetylcyclohexanone and Cyanacetamide.

p-Methylcyclohexanone yields 20 to 22 per cent. of its weight of acetylcyclohexanone as a colourless liquid distilling between 115° and 120° under 22 mm. pressure.

The condensation was brought about in the usual way. The reaction takes place within 5 or 6 minutes. The yield is about 78 per cent. of the theory. From dilute acetic acid the substance crystallises in beautiful prismatic plates darkening above 270°. (Found: N, 13·97. $C_{12}H_{14}ON_2$ requires N, 13·87 per cent.).

It is soluble in alkali but no methyl ether was obtained by treating the alkaline solution with dimethyl sulphate. Acids liberate the compound unchanged from its solution in alkali.

The hydrolysis of the condensation product was effected as usual by heating it with fuming hydrochloric acid in a sealed tube. The hydrolysed product crystallised from dilute alcohol in needles moistening at 210° and melting at 230°-232°. It is soluble in boiling water but this solution has no action on silver nitrate.

Condensation of 2-Acetylcyclohexanone and Methyl cyanacetamide.

—Ethyl methylcyanacetate was prepared from the sodium salt of ethyl cyanacetate and methyl iodide in the usual way. The ester was then treated with strong ammonia. On concentrating the ammoniacal solution and cooling, a solid mass was obtained. This was washed with ether and dried in a vacuum desiccator.

Methylcyanacetamide (1·2 g.) was dissolved in water by slightly warming. 2-Acetylcyclohexanone (1·7 g.) was then added with just enough alcohol to effect the solution of the oily diketone. Piperidine was added; the colour of the solution soon deepened.

The flask was then heated up to 65°. An appreciable quantity of a solid separated out after a short time. The flask was left overnight. Next day about 0·8 g. of the condensation product was collected and about 0·2 g. was found in the mother-liquor. Crystallised from glacial acetic acid with a few drops of water, beautiful crystals darkening above 280° were obtained. (Found: N, 14·91. $C_{11}H_{12}ON_2$ requires N, 14·89 per cent.). It dissolves in alkali to a colourless solution, from which it is precipitated unchanged by acid. It is insoluble in water and alcohol, soluble in concentrated hydrochloric acid and has properties identical with those of the condensation product obtained from 2-acetyl-*cyclo*hexanone and cynacetamide.

The same condensation product was obtained by condensing 2-acetyl*cyclo*hexanone and methylcyanacetamide in presence of sodium ethoxide. It crystallises from glacial acetic acid in beautiful long prismatic needles. (Found: N, 15·24. $C_{11}H_{12}ON_2$ requires N, 14·89 per cent.).

Condensation of 2-Methyl-2-acetylcyclohexanone and Cyanacetamide.—2-Methyl-2-acetyl*cyclo*hexanone was prepared in the following way:—Sodium salt of 2-acetyl*cyclo*hexanone was prepared by adding sodium wire to a benzene solution of the diketone, and finishing the reaction by heating under reflux on a water-bath. The sodium salt was then digested with an excess of methyl iodide in a pressure bottle for 8 hours at 70°. Sodium iodide formed was filtered off at the pump. After removing benzene from the filtrate, the residual liquid was distilled when a colourless liquid (4 g.) boiling at 130-133° under 48 mm. pressure was collected. That it was 2-methyl-2-acetyl-*cyclo*hexanone was proved by hydrolysing it with concentrated alcoholic potash when an oil was obtained, giving a semicarbazone, m.p. 195-196°. A mixture of this semicarbazone with that obtained from *o*-methyl*cyclo*hexanone also melted at 196°.

2-Methyl-2-acetyl*cyclo*hexanone (3·5 g.) was treated with cyanacetamide (2 g.) in the usual way in the presence of piperidine but no condensation product separated even after 6 hours. The flask was left overnight when on the next morning a minute quantity of a solid was collected, which dissolved in alkali. On treating this solution with dimethyl sulphate, a methyl ether was obtained melting indifferently below 155° after crystallisation from water. The mother-liquor, on dilution and acidification, became fluorescent but no other condensation product was obtained.

·Condensation of Ethyl cyclo*Hexanone Carboxylate with Cyana-cetamide: Formation of* 1 : 3 : 10-*Trioxy-4-cyano-hexahydroiso*qui*no-line* ?—The cyclohexanone carboxylate was prepared from cyclohexanone and oxalic ester according to Kötz's method (*Annalen,* 1905, **342**, 346). Its condensation with cyanacetamide was effected both by Knoevenagel's as well as by Michael's reaction. But the latter method was found to give a purer product. Cyanacetamide (2 g.) was dissolved in absolute alcohol by boiling and as crystals began to appear on cooling, sodium (0·55 g.) dissolved in absolute alcohol was added. To the sodium salt of cyanacetamide thus precipitated ethyl cyclohexanone carboxylate (4 g.) was gradually added with shaking. Soon a clear solution was obtained ; but shortly after the sodium salt had dissolved, a beautiful silky preciptiate was found in the flask and within a few minutes a thick sludge was formed. The flask being corked, was left overnight at the room temperature. Next day, water was added to make a complete solution of the sodium salt, which on acidification gave a white precipitate. This was collected and was dissolved in boiling alcohol ; from the solution which gradually turned pinkish the expected *iso*quinoline derivative separated as colourless crystals. The compound in course of time takes a pink tinge by coming in contact with air. Repeated crystallisation shows the same phenomenon. It melts with decomposition at 278-280°, sintering at 273°. [Found: N, 13·73, 13·88. $C_{10}H_{12}O_3N_2$ (*i.e.* the *iso*quinoline derivative with the aldol phase on) requires N, 13·46 per cent. Most probably a trace of the anhydro base is present which increases the percentage of nitrogen.].

The substance dissolves in alkali to form a colourless solution from which it is precipitated unchanged by acid. Ferric chloride imparts a dark greenish colour to its alcoholic solution. It is provisionally regarded as an *iso*quinoline derivative (*loc. cit.*).

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Thiosulphato-Cobalt Complexes and Complex Cobalt Thiosulphates. Part I.

By Priyada Ranjan Ray.

In spite of a voluminous work done on the double and complex thiosulphates of various metallic elements, very little attempt has been made to prepare cobalti-ammine compounds with the thiosulphate radicle either inside or outside the complex zone. One chloro-pentammine-cobaltic thiosulphate has been described by Jörgensen (*J. pr. Chem.*, 1878, [2] **18**, 212). In this the thiosulphate group occurs outside the co-ordination sphere. Following Werner's method (*Annalen*, 1911, **386**, 81) for sulphito-chloride, Duff (*J. Chem. Soc.*, 1922, **121**, 450) investigated the reaction between sodium thiosulphate and *trans*-dichloro-diethylenediamine-cobaltic chloride. On evaporating the mixed solution the complex was found to decompose with the separation of cobalt sulphide. However, he (*loc. cit.*) succeeded in preparing a thiosulphato-bromide by the interaction of carbonato-diethylene-diamine-cobaltic bromide with barium thiosulphate in a hot solution. This is the only complex cobalt compound described in literature with a thiosulphate group in the complex. The thiosulphate radicle occupies here two co-ordination positions in the complex and one of its sulphur atoms is directly linked to the central cobalt atom giving rise to the brown colour of the diethylenediaminethiosulphato-cobaltic bromide. That a sulphur atom directly linked to the central metallic atom in the complex causes the brown colour of the complex sulphito- and thiosulphato-cobalt salts has been definitely established by Werner and by Duff (*loc. cit.*). In the present paper, the preparation and properties of a number of entirely new complex thiosulphato-cobalti-ammine and cobalti-ammine thiosulphates have been described. The methods of their preparation completely differ from that adopted by Duff in the preparation of the above-mentioned thiosulphato-bromide and different methods had to be devised for different compounds

In all cases the starting material was either cobalt hydroxide, cobalt chloride or cobalt nitrate. By the action of ammonium or sodium thiosulphate and ammonia in varying strength upon the above-mentioned cobalt compounds in a current of air, the following thiosulphato-cobalti-ammine complexes and cobalti-ammine thiosulphates have been obtained.
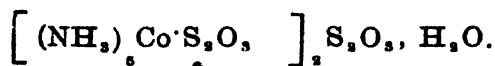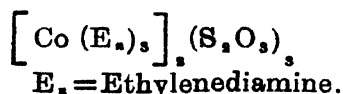
$$\left[\ (NH_3)_5\,Co\cdot S_2O_3\ \right]_2 S_2O_3,\ H_2O.$$

I

$$\left[\ Co\,(E_n)_3\ \right]_2 (S_2O_3)_3$$
$$E_n = Ethylenediamine.$$

II

$$\left[\ (NH_3)_5\,Co\cdot SO_3\ \right]_2 S_2O_3, x H_2O$$

III

$$\left[\ Co(NH_3)_6\ \right]\!\frac{Cl}{S_2O_3}$$

V

$$\left[\,SO_3\,Co\cdot(OH)\,(NH_3)_4\ \right]\cdot 2H_2O$$

IV

$$\left[\,S_2O_3\cdot Co\,(NH_3)_5\ \right]X$$
where X = Cl, Br, I or NO_3

VI

$$\left[\,S_2O_3\cdot Co\,(NH_3)_5\ \right]_2 X$$
where X = CrO_4 or S_2O_6.

VII

$$\left[\ (NH_3)_5\,Co\cdot(NO_2)\right]S_2O$$
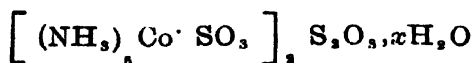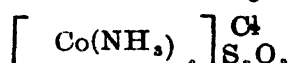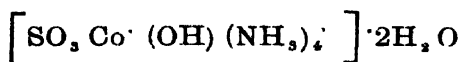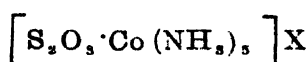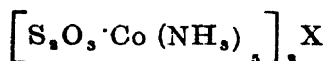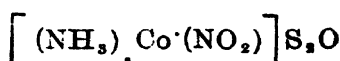
VII

The compounds I, VI and VII are all red or purple-red showing that the thiosulphate radicle is linked to the central cobalt atom directly through an oxygen atom as indicated below :—

$$\left[(NH_3)_5\ Co\text{-}O\text{-}SO_2\right]\!\!\bigg\}\!\!\begin{array}{c}S\\X\end{array}\quad or\quad \left[(NH_3)_5\ Co\text{-}O\text{-}S_2O_2\right]_2 X$$
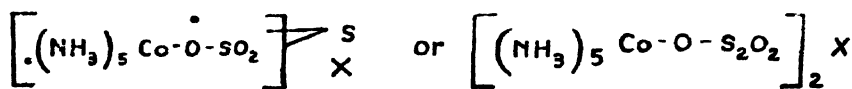
where X is either a mono-valent or a bi-valent radicle.

Compounds III and IV are yellow and hence contain a directly linked sulphur atom in the complex grouping as detailed below :—

$$\left\{\,O_3\!\!\bigg\{\!\!\begin{array}{c}\\O_2S\text{-}Co\text{-}(NH_3)_5\end{array}\!\!\right]\right\}_2 S_2O_3\ ;\ \left[(NH_3)_4\ Co\!\!<\!\!\begin{array}{c}OH\\SO_2\end{array}\!\!\bigg\}\!\!\right]O,2H_2O$$
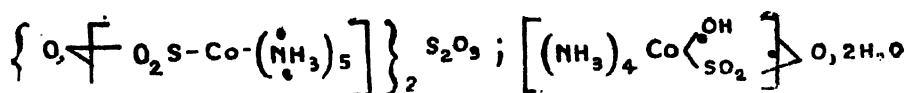
All the complex thiosulphato-compounds mentioned above belong to the monoacido-pentammine series and the thiosulphate radicle

occupies only one co-ordination position in the complex. They all form well-defined crystals and are quite stable, though in solution they hydrolyse very slowly into aquo-salts as is usually the case with mono-acido-pentammine salts in which a bivalent acid radicle occupies only one co-ordination position.

The case of sulphito-pentammine thiosulphate (III) is of special interest as it is formed from the mother-liquor after the separation of the thiosulphato-pentammine thiosulphate. Evidently a sulphite is formed in solution from the thiosulphate during oxidation or afterwards. This is discussed in detail in the experimental part.

EXPERIMENTAL.

Thiosulphato-pentammine Cobaltic Thiosulphate (I).

Cobalt hydroxide prepared from 20 g. of cobalt chloride and washed free from alkali and chlorides was mixed up with 25 g. of ammonium thiosulphate dissolved in 25 c.c. of water. The mixture was then treated with 150 c.c. of concentrated ammonia (d $0.90 =$ 25%) and thoroughly stirred. The solution was then filtered from the undissolved residue and a brisk current of air was passed through it for 3-4 hours till practically all the black crystals of oxy-cobalt compound separated in the beginning redissolved. Sometimes some purple-red crystals of the thiosulphato-pentammine separated before the disappearance of all oxy-cobalt salts. The solution was next filtered and allowed to stand overnight in a closed vessel. A thick crust of dark purple-red crystals was found at the bottom of the flask next morning. The crystals were then filtered and the filtrate was reserved. They were first washed with dilute ammonia, then with alcohol and dried in vacuo over sulphuric acid. Yield, 5-6 gms. (Found: Co, 18.58, 18.5, 18.45; S, 29.5; NH_3, 26.4, 26.58. $[S_2O_3.Co(NH_3)_5]_2S_2O_3.H_2O$ requires Co, 18.38; S, 29.9, NH_3, 26.4 per cent.).

The substance thus obtained is quite pure and can be recrystallized from aqueous ammonia. It is very sparingly soluble in water and is decomposed by mineral acids and acetic acid with liberation of sulphur dioxide and sulphur. The solution of the substance is alkaline to litmus. Silver nitrate at once gives a brownish black precipitate of silver sulphide in the cold, and the filtrate, on treating with acetic acid and warming, gives a further precipitate of silver sulphide or the filtrate after the removal of silver with ammonium

chloride, liberates sulphur dioxide and precipitates sulphur on boiling with dilute sulphuric acid. This indicates the presence of the thiosulphate both outside and inside the complex. On shaking with silver oxide however, the whole of the thiosulphate both from inside and outside the complex is removed and the alkaline solution, on heating with concentrated hydrochloric acid, gives chloropentammine chloride. This proves that the substance contains a pentammine complex. Lead acetate solution behaves like silver nitrate. Absence of sulphite and thionate was established by qualitative tests. On treating the substance with concentrated nitric acid or bromine a rose-coloured precipitate of sulphato-pentammine sulphate is obtained. The substance dissolves in dilute caustic soda solution (10 per cent.) evidently as a hydroxo-salt from which it can be precipitated unchanged by alcohol.

A better yield of the compound was obtained when instead of 150 c.c. of 25 per cent. ammonia, 250 c.c. of 12·5 per cent. ammonia was used. Thiosulphato-pentammine thiosulphate was also obtained by passing a current of air through a solution made from cobalt chloride (10 g.), ammonium thiosulphate (15 g.) and concentrated ammonia (50 c.c.). The method of procedure is exactly the same as described above, but the yield is smaller.

Tri-ethylenediamine Cobaltic Thiosulphate (II).

When the thiosulphato-pentammine thiosulphate was treated on the water bath at 60° for sometime with an excess of 10 per cent. ethylenediamine solution it was converted into a yellow, easily soluble crystalline compound. It was washed with a little water then with alcohol and finally dried in vacuo over sulphuric acid. (Found: Co, 14·1; S, 23·03; N, 20·4. $[Co(En)_3]_2(S_2O_3)_3$ requires Co, 14·1 ; S, 23·07; N, 20·2 per cent.).

Sulphito-pentammine Thiosulphate (III).

The filtrate obtained after the separation of the compound (I) was again transferred into a flask and a current of air was passed through it for several hours until the strong smell of ammonia nearly disappeared. The solution became brown and was then allowed to stand for some days being occasionally filtered from the precipitated sulphur or a little thiosulphato-pentammine salt. After a time yellowish brown crystals separated from the solution. These

were then filtered, washed with water, then with alcohol and dried in vacuo over sulphuric acid. The substance can be recrystalliéed from 5 per cent. ammonia solution. (Found: Co, 20·93, 21·0; S, 23·1, 22·95; NH$_3$, 30·3. [(NH$_3$)$_5$Co(SO$_3$)]$_2$S$_2$O$_3$ requires Co, 21·07; S, 22·86; NH$_3$, 30·3 per cent.).

A hydrated variety of sulphito-pentammine thiosulphate was obtained from the filtrate from thiosulphato-pentammine thiosulphate when after passing a current of air through the filtrate as before, the latter was treated again with concentrated ammonia liquor. A silky yellow crystalline precipitate was obtained. The crystals were washed as usual and dried in air. (Found: Co, 20·1; NH$_3$, 29·27. [(NH$_3$)$_5$Co(SO$_3$)]$_2$S$_2$O$_3$,1½H$_2$O requires Co, 20·1; NH$_3$, 29·0 per cent.).

The same substance was also obtained when a solution of carbonato-tetrammine cobaltic nitrate was mixed with an ammoniacal ammonium thiosulphate solution and the mixture was allowed to stand in a closed bottle for about a week. The yellowish brown crystals separated at the bottom of the bottle were then filtered, washed, and recrystallized from 5 per cent. ammonia solution. They were then dried as usual. On qualitative and quantitative analysis they were found to be sulphito-pentammine thiosulphate admixed with slight impurities which could not be removed by recrystallization.

The formation of sulphito-thiosulphate in all these cases presents an interesting phenomenon, where the sulphito-salt was formed in a solution to which no sulphite was previously added. It is evidently formed from the slow decomposition of ammonium thiosulphate with separation of sulphur.

$$(NH_4)_2S_2O_3 \underset{\longleftarrow}{\overset{\longrightarrow}{}} (NH_4)_2SO_3 + S.$$
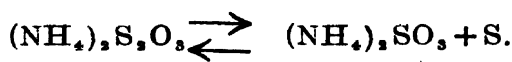
In the first two cases some ammonium sulphite might have also been formed during the oxidation of cobalt by air according to the equation:

$$(NH_4)_2S_2O_3 + 2 NH_4OH + O_2 \longrightarrow 2(NH_4)_2SO_3 + H_2O,$$
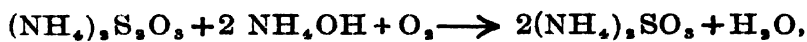
cobalt salts probably acting as a catalyst. In the last case the ammonium sulphite and thiosulphate then probably react with carbonato-tetrammine cobaltic nitrate, [(NH$_3$)$_4$Co·CO$_3$]NO$_3$ giving sulphito-tetrammine cobaltic thiosulphate, [(NH$_3$)$_4$Co·SO$_3$]$_2$ S$_2$O$_3$, which in presence of ammonia leads to the formation of the

pentammine sulphito-thiosulphate. This is supported by the fact already stated that the pentammine sulphito-thiosulphate can also be obtained by the addition of strong ammonia to the filtrate from thiosulphato-thiosulphate, which has become too poor in ammonia and does not separate the sulphito-pentammine salt by itself.

The sulphito-thiosulphate is alkaline to litmus, more or less sparingly soluble in water, dissolves in cold caustic alkali to an orange brown solution. A solution of the salt with silver nitrate solution gives a brownish black precipitate of silver sulphide in the cold; the filtrate on boiling with acetic acid or dilute sulphuric acid liberates sulphur dioxide without any separation of silver sulphide, but grey metallic silver is only precipitated. Lead acetate solution behaves in a similar fashion. Absence of thionates and sulphates and the presence of sulphites and thiosulphates were also definitely proved by qualitative tests after removing the cobalt as sulphide with sulphuretted hydrogen from an ammoniacal solution of the salt and then removing the excess of sulphuretted hydrogen by cadmium carbonate. When shaken vigorously with silver oxide, a strongly alkaline brown solution was obtained, which after filtration and evaporation with concentrated hydrochloric acid, gave characteristic crystals of chloropentammine chloride.

Hydroxo-tetrammine Cobaltic Sulphite (IV).

The sulphito-pentammine thiosulphate was dissolved in 5 per cent. caustic soda solution to a clear orange-coloured liquid which on treatment with alcohol gave a precipitate of copper-coloured beautiful silky plates. These were first washed with 30 per cent. alcohol and then with absolute alcohol. The crystals were then dried in vacuo over calcium chloride. (Found : Co, 22·6; S, 12·0; NH_3, 26·0. $[(NH_3)_4 \cdot Co \cdot (OH)SO_3]$ $2H_2O$ requires Co, 22·7; S, 12·3; NH_3, 26·1 per cent.).

The substance is readily soluble in water and is strongly alkaline to litmus and precipitates silver oxide from a solution of silver nitrate. It does not react with potassium ferrocyanide, potassium ferricyanide and potassium chromate solution. With barium chloride solution a white turbidity appears which gradually increases on keeping and after sometime a black precipitate of cobaltic oxide is formed. All these properties indicate that the substance is a hydroxo-compound. It readily absorbs carbon dioxide and forms a carbonate.

A compound of the composition $Co(NH_3)_4SO_3.OH, 3H_2O$ has been described by Hofmann and Reinsch (*Zeit. anorg. Chem.*, **16**, 384). They prepared it by the action of silver oxide upon a solution of sulphito-aquo-tetrammine cobaltic thiocyanate and represented it as sulphito-aquo-tetrammine cobaltic hydroxide $[Co(NH_3)_4 H_2O.SO_3]$ OH, $2H_2O$. But it is very unlikely that an aquo-salt can be formed in the present case from a strongly alkaline solution. Of course in aqueous solution all hydroxo-compounds are hydrolysed into aquo-hydroxides and behave as such. The compound could also be represented as $[(NH_3)_4.Co.(SO_3)]OH.2H_2O$; but its method of formation from a pentammine salt with evolution of one molecule of ammonia as well as the usually greater tendency of the sulphito group to occupy only one co-ordination position in the complex (the number of sulphito-compounds in which the sulphito-group occupies one co-ordination position is much larger than those in which it occupies two) strongly suggest the constitution (IV) given above. The reaction leading to its formation can be represented as below :—

$$[(NH_3)_5 Co\cdot SO_3]_2 S_2O_3 + 2KOH \longrightarrow 2[NH_3)_5 Co\cdot SO_3]OH + K_2S_2O_3$$

$$\downarrow$$

$$2[(NH_3)_4\cdot Co\cdot (OH)SO_3] + 2NH_3.$$
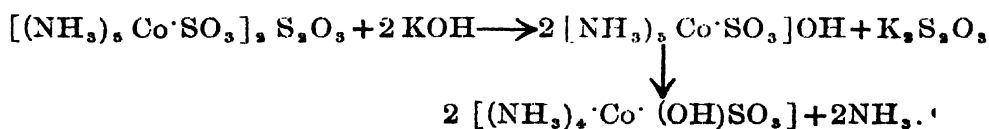
Hexammine Cobaltic Chloro-thiosulphate (V).

Crystallized cobalt chloride (10 g.), ammonium chloride (10 g.) and sodium thiosulphate (24 g.) were dissolved in water (50 c.c.) and treated with ammonia (120 c.c., d 0·90). The solution was filtered and a brisk current of air was passed through it for a few minutes. Yellow crystals began to separate at once but the mixture was allowed to stand over-night. Next morning the crystals were separated by filtration from the mother-liquor and purified by recrystallization from 4 per cent. ammonia solution. The crystals were first washed with 20 per cent. alcohol containing a little ammonia and then with absolute alcohol. They were dried in vacuo over calcium chloride. Yield 8 g. approximately. In serves as an excellent method for preparing hexammine salts. (Found : Co, 18·52; S, 20·65; Cl, 11·1; NH_3, 32·7. $[Co(NH_3)_6]ClS_2O_3$ requires Co, 19·1: S, 20·71; Cl, 11·3; NH_3, 33·0 per cent.).

The substance forms beautiful silky yellow crystals, fairly soluble in water. The solution can be boiled without decomposition. It

gives all the characteristic reactions for hexammine salts. The whole of the thiosulphate and chlorine are precipitated by silver nitrate solution in the cold.

Thiosulphato-pentammine Cobaltic Chloride (VI).

Hydrated cobalt chloride (10 g.) dissolved in the least quantity of cold water was mixed with ammonium chloride (24 g.) and sodium thiosulphate (12 g.). To the solution 60 c.c. of 7 per cent. ammonia were added. The solution was filtered and a rapid current of air was passed through the filtrate for an hour and a half, the solution being cooled in ice water all the while. Purple-red crystals separated in large quantities. The mixture was allowed to stand for about two hours in the cold. The crystals were then filtered and washed with 2 per cent. ammonia solution. The crystals thus obtained were contaminated with some thiosulphato-pentammine thiosulphate, which could not be removed by simple recrystallization. They were therefore dissolved in the least amount of water and then salted out by the addition of a saturated solution of ammonium chloride. The crystals were separated, washed first with ammoniacal water and then with alcohol. They were dried as usual in vacuo over sulphuric acid. (Found: Co, 20·3 ; S, 22·15; Cl, 12·25; NH_3, 29·16. [$S_2O_3Co(NH_3)_5$] Cl requires Co, 20·24; S, 21·96; Cl, 12·18; NH_3, 29·16 per cent.).

The substance thus prepared has a dark red colour and is fairly soluble in water. Silver nitrate solution gives a precipitate of silver chloride from its solution in the cold; the filtrate on boiling with dilute sulphuric acid gives a black precipitate of silver sulphide. These reactions prove that the chlorine is in the outer zone and the thiosulphate group is in the inner zone of the complex. With concentrated hydrochloric acid in the cold it is transformed into chloropentammine cobaltic chloride.

Thiosulphato-pentammine Bromide.

To a cold strong solution of the above thiosulphato-chloride, a saturated solution of sodium bromide was added. Dark red crystals of the bromide separated out. These were washed and dried as in the case of the chloride. (Found: Co, 17·84; Br, 24·1. [$S_2O_3 \cdot Co(NH_3)_5$] Br requires Co, 17·6; Br, 23·8 per cent.). The aqueous solution in the cold gives a precipitate of silver bromide with silver nitrate solution. The filtrate on boiling with dilute sulphuric acid gives a black precipitate of silver sulphide.

Thiosulphato-pentammine Iodide.

To a cold strong solution of the chloride, crystals of potassium iodide were added. The dark red crystalline precipitate thus obtained was washed and dried as usual. (Found: Co, 15·54; I, 33·67. $[S_2O_3.Co.(NH_3)_5]$ I requires Co, 15·4; I, 33·2 per cent.).

An aqueous solution of the substance in the cold gives a yellowish precipitate of silver iodide with silver nitrate solution. In the filtrate the thiosulphate can be detected as above.

Reactions of the Thiosulphato-pentammine Cobaltic Ion.

A solution of the thiosulphato-pentammine cobaltic chloride gives a red precipitate with potassium ferrocyanide solution and a chocolate-brown precipitate with the ferricyanide solution. With potassium stanni-chloride it forms red crystals of the thiosulphato-pentammine stanni-chloride which is readily hydrolysed by water. With sodium platinichloride it gives an insoluble brown platini-chloride. With mercuric chloride solution a voluminous light-rose-coloured precipitate is obtained.

Thiosulphato-pentammine Cobaltic Nitrate (VI).

Crystalline cobalt nitrate (12 g.), ammonium nitrate (15 g.) and sodium thiosulphate (24 g.) were dissolved in water (50 c.c.) and treated with strong ammonia (120 c.c., d 0·90). The solution, after filtration, was treated with a rapid stream of air for about two hours and it was filtered from any black oxycobalt salts. Air was again passed through the filtrate for about an hour till dull purple-red crystals began to separate. The mixture was then allowed to stand overnight in the cold. Next morning the crystals were collected, washed with cold ammoniacal water and recrystallized from hot 4 per cent. ammonia solution. The substance was again washed with aqueous alcohol contaning a little ammonia, then with alcohol and afterwards dried in vacuo over calcium chloride. (Found: Co, 18·5, 18·7; S, 20·5; N, 26·77, NH_3,26·73. $[Co(NH_3)_5S_2O_3]$ NO_3 requires Co, 18·55; S, 20·12; N, 26·4; NH_3, 26·7 per cent.).

The substance is sparingly soluble in water; it gives no precipitate with silver nitrate solution in the cold but on keeping for sometime the solution gradually turns turbid and finally a black precipitate of silver sulphide appears. On treatment with silver oxide the whole

of the thiosulphate is removed; the filtrate, after the removal of the excess of silver with hydrochloric acid and on evaporation with strong hydrochloric acid, gives characteristic crystals of chloropentammine chloride. . The presence of nitrate group was established by qualitative tests. That the substance is a thiosulphatopentammine cobaltic nitrate is further confirmed by converting it into a dithionate as described below.

Thiosulphato-pentammine Cobaltic Dithionate (VII).

To a strong solution of the thiosulphato-nitrate in 4 per cent. aqueous ammonia, a concentrated solution of sodium dithionate was added. On cooling well-defined purple-red crystals separated out. These were washed with water and then with alcohol and dried as usual in vacuo over sulphuric acid. (Found: Co, 17·69; S, 28 85; NH_3, 25·27; N, 21 5. [$(NH_3)_5Co.S_2O_3$], S_2O_6 requires Co, 17·55; S, 28·57; NH_3, 25·3; N, 20·83 per cent.).

The substance is sparingly soluble in water. Silver nitrate solution gives no immediate precipitate in the cold but, on keeping, the solution becomes turbid and finally a black precipitate of silver sulphide appears ; but the precipitation does not become complete even after an hour.

Thiosulphato pentammine Chromate (VII).

To a concentrated solution of the thiosulphato-pentammine chloride in the cold a saturated solution of potassium chromate was added. Brilliant silky leaflets separated after a time. These were washed with dilute ammonia and recrystallized from hot dilute ammonia (2 per cent.). The product was washed and dried as usual. (Found: Co, 18·6; Cr, 8·44. [$(NH_3)_5CoS_2O_3$]$_2$ CrO_4 requires Co, 18·8 ; Cr, 8·28 per cent.).

It forms red silky crystals, very sparingly soluble in water. An aqueous solution in the cold gives a red precipitate of silver chromate with silver nitrate solution. The filtrate from silver chromate gives all characteristic reactions for thiosulphuric acid.

Nitropentammine Thiosulphate (VII).

Cobalt hydroxide from 10 g. of cobalt chloride crystals was mixed up with ammonium thiosulphate (20 g.) and sodium nitrite (14 g.)

dissolved in a small quantity of water. The mixture was then poured down into 90 c.c. of 25 per cent. ammonia and a rapid current of air was passed through the mixture for about 3 hours. It was then filtered and the filtrate was allowed to stand overnight. A large crop of brownish yellow crystals was found at the bottom of the vessel next morning. These were filtered, washed and recrystallized from dilute ammonia. The product thus obtained is bright yellow in colour. (Found: Co, 19·74 ; S, 21·05, 21·55 ; N, 28·5; NH_3, 28·3. $[(NH_3)_3 Co. NO_2]$ S_2O_3 requires Co, 19·5 ; S, 21·2 ; N, 27·81 ; NH_3, 28·14 per cent.).

It is sparingly soluble in water. The solution gives immediately a black precipitate of silver sulphide with silver nitrate solution. The filtrate on treatment with sulphuric acid and warming gives out nitrous fumes.

Method of Analysis.

In the above compounds cobalt was always estimated, except in the case of the thiosulphato-chromate, as cobalt sulphate by evaporating with sulphuric acid. Sulphur was estimated as barium sulphate by oxidizing the sulphites, thiosulphates or dithionates with ammoniacal hydrogen peroxide. Chromium in the case of the thiosulphato-chromate was estimated volumetrically after igniting the compound and then fusing it with sodium peroxide. Ammonia was estimated by distillation. In some cases total nitrogen was estimated by combustion. The halogen elements were estimated as their silver salts as usual after oxidizing the compounds with ammonical hydrogen peroxide to convert the thiosulphates into sulphates. Cobalt in the thiosulphato-chromate was estimated by precipitating as cobalt rubeanate after removing the chromium as chromate by boiling with caustic soda and then dissolving the cobaltic oxide with hydrochloric acid. The solution of the cobalt chloride thus obtained was then neutralized with ammonia, treated with sodium acetate and an alcoholic solution of rubeanic acid was added in excess to precipitate the cobalt. The cobalt rubeanate was finally converted into cobalt sulphate by treatment with a mixture of nitric acid and sulphuric acid and weighed as such. (Râv and Ray, This *Journal*, 1926, **3**, 124).

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The Influence of Substituents on the Stability of Schiff's Bases. Part I. Hydrolysis of Nitro- and Methoxy-benzylidene Anilines.

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Apart from the work of Reddelien and Danilof (*Ber.*, 1921, **54** [B], 3132) on the fission of a few aromatic keto-anils, little is known regarding the influence of substituents on the stability of Schiff's bases in general. Their results may be summarised in the general expression that the hydrolysis of anils by mineral acids in aqueous solution is facilitated by "positive" groups, such as NH_2, NRR', and retarded by "negative," such as NO_2, $COOH$ in the *para*-position to the nitrogen atom in the aniline residue. *Ortho*-substituents seem to exert steric hindrance. The cases examined by them, however, do not seem to be strictly comparable and no satisfactory attempt has been made to distinguish between the various factor that may influence the double bond in the system $>C=N-$.

For this reason, a systematic investigation of the derivatives of benzylidene aniline has been instituted with the object of differentiating between the following possible factors: (1) general polar effect; (2) induced polar effect; (3) effect of mass; (4) steric influence; (5) effect of conjugation, and (6) effect of constitutional changes.

In this communication, the hydrolysis of benzalaniline and the three nitro- and three methoxy-benzylidene anilines is described and the results are discussed.

EXPERIMENTAL.

Preparation of the Anils.

Benzylidene aniline was prepared by mixing together equal quantities of benzaldehyde and aniline without the application of heat; colourless needles from methyl alcohol, m. p. 53° ; yield almost quantitative (Michælis, *Ber.*, 1891, **24**, 750).

The nitro- and methoxy-benzylidene anilines were prepared in the usual way. The m-*methoxy-benzylidene aniline*, purified by repeated fractional distillation in vacuo, is a light yellow viscous liquid, b. p. 206-207° at 20 mm., (Found: C, 79·8; H, 6·3; N, 6·7. $C_{14}H_{13}NO$ requires C, 79·6; H, 6·2; N, 6·6 per cent.). The o-*methoxy-benzylidene aniline* distilling at 204-205° at 25 mm., solidified in a freezing mixture. It was further purified by crystallising from light petroleum in colourless needles, m. p. 33-34°, which is about 10° lower than the m. p. given by Noelting (*Ann. Chim. Phys.*, 1910, (viii), **19**, 476). (Found: C, 79·7; H, 6·2; N, 6·7 per cent.). The *para* compound crystallises in colourless plates from light petroleum, m. p. 62·5-63·5° (Noelting, *loc. cit.*).

Hydrolysis of the Anils.

Equivalent quantities of the anils (1·2 g. of benzalaniline, 1·4 g. of a methoxy- and 1·5 g. of a nitro-derivative) were separately dissolved in a half-litre stoppered separating funnel in 300 c. c. of ligroin (b. p. 100-120°) and 75 c.c. of N/10 hydrochloric acid were then added to each. The funnels were shaken mechanically in a room the temperature of which remained at 16-18°. The liquids had been left in the room for a few hours previous to mixing so as to attain the temperature of the room. It was found that variations of temperature within this range did not materially affect the amount of anil hydrolysed. The shaking was carried out for varying periods of time, and at the end of each period the acid layer was quickly drawn off and diluted to 100 c.c. with water. Three 25 c.c. portions of the diluted solution were withdrawn, mixed with excess of dilute hydrochloric acid, cooled in ice, and titrated with N/5 sodium nitrite, using starch-iodide paper as indicator. The results of the second and third titrations, in the few cases in which they were not identical, did not differ by more than 0·2 c.c.; the mean was taken as the correct result. The sodium nitrite solution was standardised against a freshly made solution of pure aniline in hydrochloric acid. The results (from 140 experiments) are tabulated below.

Ligroin proved to be the most suitable of the common organic solvents, Blank experiments showed (a) that when a ligroin solution of an aldehyde, or its anil, is shaken with water, the aqueous solution after separation does not require more than one

drop of the sodium nitrite solution to produce a blue colour on starch-iodide paper, and (b) that an aqueous solution of aniline hydrochloride when shaken with ligroin remains unaltered in strength. Further, the separation of the two layers, even after prolonged shaking, is almost instantaneous, no emulsion being formed. It is, therefore, reasonable to suppose that the quantitative data obtained by these experiments are strictly comparable.

Percentages of Anils Hydrolysed.

	1	2	3	4	5	6	7
Time in hours.	ord. anil.	*para* nitro-	*meta* nitro-	*ortho* nitro-	*para* methoxy-	*meta* methoxy-	*ortho* methoxy-
1	58·4	32·8	35·7	21·2	81·8	54·0	78·8
2	75·2	47·4	51·1	32·8	87·6	69·3	82·5
4	80·3	65·7	67·2	55·4	88·3	84·7	84·7
8	85·4	69·3	70·0	62·8	88·3	84·7	84·7
18	90·5	75·2	75·2	65·7			
24	90·5	75·2	75·2	65·7			

Discussion of the Results.

A glance at the results shows that the reaction is reversible. Further, although from a polar point of view the substituent groups are opposite in character, the equilibrium points of the nitro- and methoxy-anils (maximum 75·2 per cent. for *p*- and *m*-nitro- and 88·3 per cent. for *p*-methoxy-) are distinctly lower than that of the parent substance. This result may be due to the effect of mass, but experiments have yet to be carried out with derivatives in which the substituents are of the same order of polarity but vary in mass.

The initial velocities of hydrolysis are in the order : methoxy-anils > parent substance > nitro-anils (except in the case of *m*-methoxy anil), which may be attributed primarily to the general polar influence of the substituent groups.

The initial velocities of hydrolysis of the isomerides, *para* and *meta*, are in the order: $m > p$ for the nitro-, and $p > m$ for the methoxy-anils. In the former case the difference, though small, is sufficiently above the range of experimental error. It is interesting to notice that the order of alternation is in agreement with the principles of induced alternate polarity as represented by the following formulae, oxygen being taken as the " key " atom :
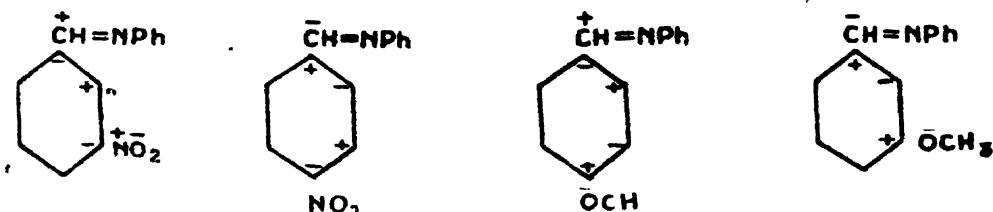
(Compare Lapworth, Shoesmith, and others, *J. Chem. Soc.*, 1922, **121**, 1392; 1923, **123**, 2838; 1924, **125**, 1312, 2278, on the hydrolysis and reduction of various substituted benzyl bromides).

The two nitro-derivatives. however, have the same equilibrium point, and even in the case of the two methoxy anils, the initial difference of 27·8 has been reduced to only 3·6 per cent. when equilibrium is reached. This would indicate that the influence of induced polarity is exerted *primarily* on the velocity.

In the case of *m*-methoxy anil, whose initial velocity of hydrolysis is lower than that of the parent substance, the general and the induced polarity are competing against each other. This result may, however, be attributed partly to this condition but not entirely, as it cannot be assumed that the effect of induced polarity is greater than the general polar effect. The question therefore must be left open until more cases of a similar nature have been examined.

The low initial velocity and equilibrium point of *o*-methoxy anil in comparison with the para compound may reasonably be attributed to steric influence, without neglecting to take into account the possible effect of conjugation as represented by the formula :
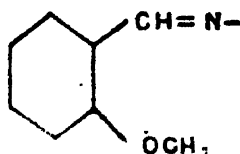
In the case of the two corresponding nitro-derivatives, however, the differences are much greater and in this connexion it should be mentioned that in addition to spatial influence there is the possibility of incipient structural alteration such as was demonstrated by Sachs and Kempf (*Ber.*, 1902, **35**, 2707. Compare also Ciamician and Silber, *Ber.*, 1901, **34**, 2040).
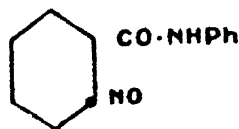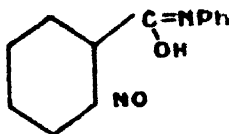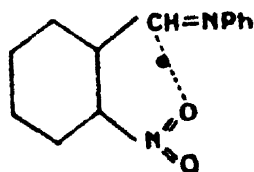
<p style="text-align:center">Conclusion.</p>

Dimroth and Zoeppritz (*Ber.*, 1902, **35**, 984) have shown that the formation and fission of anils should be regarded as additive reactions, *viz.*,

$$PhCHO + NH_2Ph \; \underset{\longleftarrow}{\longrightarrow} \; PhCHOH\cdot NHPh \; \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} \; PhCH=NPh.$$
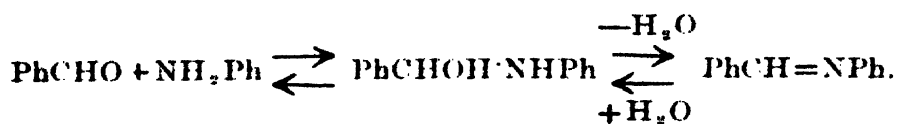
It follows, therefore, that any conclusion that may be drawn from this work might be equally applicable to additive reactions in general. Reference may be made here to the two general principles tentatively advanced by E. H. Ingold (*J. Chem. Soc.*, 1925, **127**, 469) in connexion with the Michael addition reaction, *viz.*,

(1) "*The primary effect of polar conditions is on the velocity of reversible additions.*"

(2) "*The primary effect of spatial conditions is on the equilibrium in reversible additions.*"

The results now obtained support the first principle as regards both general and induced polar conditions and the second only partially (see the figures for *p*- and *o*-methoxy-anil). Work to elucidate this point is in hand.

A New Method for the Preparation of 4-Acetylamino-3-chloro-aniline.

By Sudhir Chandra Niyogy.

4-Acetylamino-3-chloro-aniline, which is used in preparing substances that are of value in medicine, was prepared by Cain (*J. Chem. Soc.*, 1909, **95**, 716). As his method was found to be imperfect it was decided to ascertain the necessary details.

The starting point in the preparation of the substance is *p*-nitraniline. The first step is the chlorination of *p*-nitraniline so as to obtain 2-chloro-4-nitraniline, which is then acetylated and subsequently reduced.
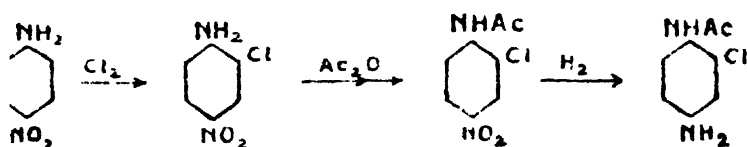
There are many methods for the preparation of 2-chloro-4-nitraniline (*Annalen*, 1876, **182**, 108; *Ber.*, 1894, **27**, 377; *J. Chem. Soc.*, 1908, **93**, 1773; *Chem. Zentz*, 1900, II, 360). All these may be broadly divided into two classes : (1) Chlorination in concentrated mineral acid solution; (2) chlorination in dilute mineral acid solution. The chlorinating agent employed are (1) chlorine gas, (2) sodium hypochlorite, and (3) bleaching powder.

Careful repetition of Flurscheim's method for the preparation of 2-chloro-4-nitraniline (*J. Chem. Soc.*, 1908, **93**, 1773) showed that the author's claims are exaggerated, as the formation of tarry matter is very considerable. On following the specification of Cassella and Co's Patent (D. R. P., 109189) the product obtained was invariably 2:6-dichloro-4-nitraniline even when only half the required quantity of chlorine was used.

Sodium hypochlorite, and bleaching powder containing a known weight of available chlorine, were next employed without any better result. The corresponding bromo-derivative is very easily prepared by the addition of the required quantity of bromine in acetic acid

*solution to an acetic acid solution of p-nitraniline at ordinary tempe-
rature. But when the experiment was repeated using acetic acid
containing a known weight of chlorine, the result was indifferent.
As the result of this series of experiments it may be safely concluded
that all common methods of preparing 2-chloro-4-nitraniline are
either faulty or misleading.*

In one experiment p-nitro-acetanilide was boiled with hydro-
chloric acid to hydrolyse the anilide, and the acid solution was cooled
with ice and treated with chlorine. A yellowish brown product
separated which, on purification, had m.p. 103—4°, the m.p. of
2-chloro-4-nitraniline being 104-5°. So this was the required com-
pound. The main difference in this experiment is the presence of
acetic acid and assuming that this is somehow favourable to the
formation of 2-chloro-4-nitraniline, a series of experiments was
made using varying proportions of acetic acid, hydrochloric acid and
water, till the experimental conditions were so adjusted as to give
a yield of 8·5 g. of 2-chloro-4-nitraniline from 10 g. p-nitraniline.

The failure of the previous experiments may be accounted for as
follows :—If during the chlorination, a solvent (like hydrochloric
acid, sulphuric acid or a mixture of hydrochloric acid and acetic
acid) is employed in which p-nitraniline as well as 2-chloro-4-nitra-
niline is soluble, the resulting product is invariably the dichloro
compound. But if a solvent is employed in which p-nitraniline is
soluble but not the 2-chloro-4-nitraniline, the latter separates as soon
as it is produced and escapes further chlorination. The best yield
obtained amounted to about 70% of the theory. Some decomposition
invariably takes place and some of the dichloro-compound is
invariably formed.

The reduction of 4-acetylamino-3-chloro-1-nitrobenzene was
effected by Cain (*loc. cit.*) using acetic acid and iron filings. The
reduction product obtained by me was different from Cain's product.
Cain's sample was yellow needles, m.p. 111°, and was moderately
soluble in water. The product (empirical formula, $C_8H_9ON_2Cl$)
obtained by me had a very faint pink colour (which darkened on
exposure to sunlight) and melted at 134-35°. It was very soluble
in water and gave the following reactions :—

    (1) It gave the diazo reaction and therefore contains a free
        amino group.

    (2) When dissolved in dilute hydrochloric acid, it does not
        give the indamine test for p-diamines ; when it is

heated for some time with concentrated hydrochloric acid, it gives this test.

Thus one is led to conclude that the compound having a m.p. 134—35° is 4-acetylamino-3-chloraniline. Cain must have been misled by some experimental error.

EXPERIMENTAL.

2-Chloro-4-nitraniline.

p-Nitraniline (10 g.) was dissolved in water (360 c.c.) containing hydrochloric acid (50 c.c. 37%) and glacial acetic acid (25 c.c.). The solution was cooled to a temperature of 10—15° and a slow current of chlorine was passed through the liquid with constant stirring. (If the current of chlorine is rapid, the quantity of tarry matter formed is considerable.) A yellow precipitate separated which was filtered off from time to time. The end of the reaction is very easily ascertained : when all the nitraniline had been used up, chlorine begins to escape. The combined solid product was boiled with water when a tarry mass settled down. Rectified spirit was then added in small quantities at a time to the boiling liquid, till the residue had a granular appearance. The whole was then filtered rapidly and the filtrate was largely diluted with water when 2-chloro-4-nitraniline separated as a yellow flocculent precipitate. As the compound is somewhat soluble both in water and in dilute alcohol, the filtrate was cooled in ice water. The precipitate was collected and dried; m.p. 103·4°. Yield 8·5 g.

Acetylation of 2-Chloro-4-nitraniline.

2-Chloro-4-nitraniline (10 g.) was dissolved in glacial acetic acid (80 c.c.) and acetic anhydride (45 c.c.) was added. Sulphuric acid (20 drops) was added to it with shaking. After an hour the solution was poured into boiling water (600 c.c.). On cooling, light brown crystals separated, m. p. 139—40°. Yield 9 g. In the absence of sulphuric acid the acetylation is far from being complete (cf. however, Orton, J. Chem. Soc., 1908, 93, 1242).

1-Amino-4-acetylamino-3-chlorobenzene.

Iron dust (5 g.), glacial acetic acid (2 c.c.) and water (50 c.c.) were placed in a round bottom flask. 4-Acetylamino-3-chloro-1-

nitro-benzene (5 g.) was taken and half of it was at once added to the contents of the flask and thoroughly mixed by shaking. The mixture became warm but in no case did the temperature rise higher than 50°. Further quantities of the nitro-compound were added gradually to this warm mixture. After all the nitro compound had been added, the mixture was shaken till it reached its initial temperature. The mixture was then gently boiled with a solution of sodium carbonate (2 g.) in water (10 c.c.) and filtered hot at the pump. The residue was twice extracted with small quantities of water and filtered hot. The combined filtrates, on cooling, gave a light pink precipitate, m. p. 125-28°. It was recrystallised from benzene, m.p. 134-35°. Yield 3·2 g. (Found: N, 15·21 ; Cl, 19·74 ; C, 52·1 ; H, 5·2. $C_8H_9ON_2Cl$ requires N, 15·18 ; Cl, 19·24 ; C, 52·03 ; H, 4·8 per cent.).

My thanks are due to Prof. H. K. Sen for the kind interest he has taken in this work.

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Studies in the Thiosemicarbazone Series.

By

Prafulla Kumar Bose and Dhirendranath Ray Chaudhury.

The hydrazones of $\alpha\beta$-unsaturated aldehydes and ketones, as a rule, undergo pyrazoline conversion either spontaneously or when their solutions in suitable solvents are heated for sometime. Thus the phenylhydrazones of acraldehyde and mesityl oxide change into phenyl pyrazoline and trimethyl phenyl pyrazoline respectively (Fischer and Knoevenagel, *Annalen*, 1887, **239**, 194; *J. pr. Chem.*, 1894, (2), **50**, 531; *cf.* Kishner, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 987, 957). Benzal-acetophenone phenylhydrazone is transformed into 1 : 3 : 5-triphenyl-pyrazoline in warm alcoholic solution (Knorr and Laubmann, *Ber.*, 1888, **21**, 1205). Similarly cinnamylidene phenylhydrazone, in hot glacial acetic acid solution, is converted into 1 : 5-diphenyl pyrazoline (Auwers and Muller, *Ber.*, 1908, **41**, 2697), although Bauer and Dieterle (*Ber.*, 1911, **44**, 2697) found that the reaction of Auwers is not a general one. The change takes place by the migration of the secondary hydrogen atom to the unsaturated part, CH=CH of the ketone or aldehyde, thus :—

$$
\begin{array}{ccc}
\text{CH—CH} & & \text{CH}_2\text{·CH} \\
\| \quad \| & \longrightarrow & | \quad \| \\
\text{C}_6\text{H}_5\text{·CH} \quad \text{N} & & \text{C}_6\text{H}_5\text{·CH} \quad \text{N} \\
/ & & \vee \\
\text{HN·Ph} & & \text{N·Ph}
\end{array}
$$

$$\text{(I)}$$
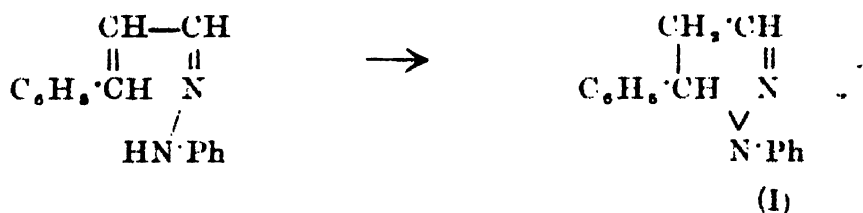
that is, the open-chain system $-\text{CH}=\text{CH·CH}=\text{N}-\text{NH}-$ is potentially capable of ring closure.

The present investigation was undertaken with a view to examine whether the thiosemicarbazones of unsaturated aldehydes and ketones, which contain the necessary reactive groupings, would similarly undergo pyrazoline conversion, thus :

$$
\begin{array}{ccc}
\text{CH—CH} & & \text{CH}_2\text{·CH} \\
\| \quad \| & \longrightarrow & | \quad \| \\
\text{C}_6\text{H}_5\text{·CH} \quad \text{N} & & \text{C}_6\text{H}_5\text{·CH} \quad \text{N} \\
/ & & \vee \\
\text{HN·CS·NHR} & & \text{N·CS·NHR}
\end{array}
$$

$$\text{(II)}$$
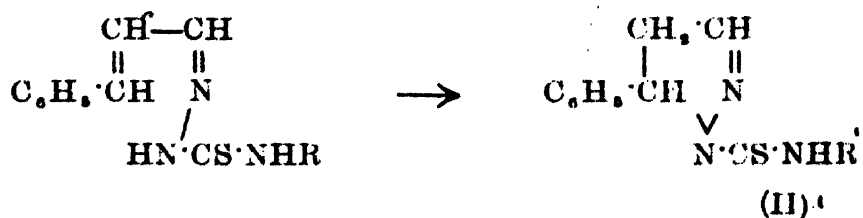
For this purpose cinnamylidene thiosemicarbazone was heated in glacial acetic acid solution for a few hours but the expected transformation did not occur. Assuming that the substituents of the thiosemicarbazides in position 4, as well as those in the unsaturated aldehyde might have some favourable influence on the above course of reaction, several 4-substituted thiosemicarbazides have been condensed with cinnamic aldehyde and benzalacetone in alcoholic or glacial acetic acid solution. Each of the thiosemicarbazones thus obtained was heated in glacial acetic acid with a view to obtain the expected pyrazoline derivative. But the intramolecular transformation was not observed to take place.

The inability of the imino hydrogen atom to saturate the ethylenic double bond may be attributed to the constitution (III) depicted below, where the hydrogen atom, having migrated over to the S-atom, is no longer available for the pyrazoline transformation (cf. Wilson and Burns, J. Chem. Soc., 1922, **121**, 870; also Bose, J. Indian Chem. Soc., 1925, **2**, 98). In fact the thiosemicarbazones possess acidic properties, and dissolve in cold caustic alkalis thus supporting the above supposition.

$$C_6H_5 \cdot CH : CH \cdot CH : N \cdot NH \cdot CS \cdot NHR$$
$$\longrightarrow C_6H_5 \cdot CH : CH \cdot CH : N \cdot N : C(SH).NHR$$

(III)
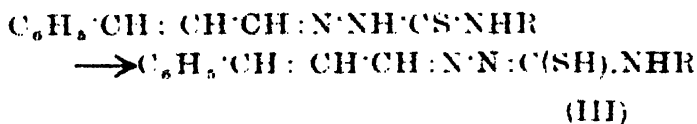
The thiosemicarbazones are crystalline substances most of which are pale yellow in colour. When heated with caustic soda, they first dissolve and then decompose liberating the original aldehyde or ketone. Freshly prepared yellow mercuric oxide is coloured black in a minute when an alcoholic solution of the thiosemicarbazone is warmed with it on the water-bath. They produce yellow crystalline precipitates with mercuric chloride in alcoholic solution.

Cinnamylidene benzyl dithiocarbazinate and the product from benzal acetone and benzyl dithiocarbazinate behave similarly. They, however, dissolve in cold alkalis with great difficulty and unlike the thiosemicarbazones are not easily desulphurised by freshly precipitated mercuric oxide. On boiling with alkali for sometime, they decompose, the smell of original aldehyde or ketone being perceptible at the same time.

A General Method for the Preparation of Thiosemicarbazones in Glacial Acetic Acid.

Molecular proportions of cinnamic aldehyde or benzal acetone and thiosemicarbazides are heated in glacial acetic acid solution over a flame. The time required for the preparation of cinnamic aldehyde thiosemicarbazones is about 15 minutes, whereas in the case of the ketone about half an hour is found to be necessary. The condensation products crystallise out on concentrating the solution, and can be purified by recrystallisation from suitable solvents.

Cinnamylidene-4-methylthiosemicarbazone crystallises from benzene by the addition of ligroin in yellow needles melting at 170°. It is fairly soluble in benzene, carbon disulphide, pyridine, acetone and acetic acid but insoluble in ligroin. (Found: S, 14·69. $C_{11}H_{13}N_3S$ requires S, 14·60 per cent.).

Cinnamylidene-4-ethylthiosemicarbazone was crystallised from benzene by the addition of ligroin, in pale yellow needles. It melts at 166-167°. It is soluble in all common solvents except ligroin. (Found: S, 13·59. $C_{12}H_{15}N_3S$ requires S, 13·7 per cent.).

Cinnamylidene-4-phenylthiosemicarbazone has been described (Pulvermacher, *Ber.*, 1894, **27**, 617) as having a melting point 175-176°, but our product, when crystallised from pyridine, melted at 182-183°. (Found: N, 15·01. $C_{16}H_{15}N_3S$ requires N, 14·95 per cent.).

Cinnamylidene-4-p-tolylthiosemicarbazone crystallises from alcohol in pale yellow crystals which melt at 194°. It is moderately soluble in all solvents. (Found: N, 14·24. $C_{17}H_{17}N_3S$ requires N, 14·10 per cent.).

Cinnamylidene-4-m-tolylthiosemicarbazone comes out from alcohol in almost colourless crystals, m.p. 146°. It is highly soluble in pyridine and acetone but moderately in alcohol and acetic acid. (Found: N, 14·4. $C_{17}H_{17}N_3S$ requires N, 14·20 per cent.).

Cinnamylidene-4-β-naphthylthiosemicarbazone crystallises from a mixture of alcohol and pyridine in almost colourless needles, m.p. 213° with decomposition. It is highly soluble in pyridine, moderately in alcohol and sparingly in benzene, chloroform or glacial acetic acid. (Found: S, 9·22. $C_{20}H_{17}N_3S$ requires S, 9·6 per cent.).

Benzalacetone-thiosemicarbazone was crystallised from glacial acetic acid in pale yellow needles melting at 147-148°. It is fairly

soluble in benzene, chloroform, glacial acetic acid, alcohol, acetone and pyridine. (Found: N, 19·05. $C_{11}H_{13}H_3S$ requires N, 19·18 per cent.)-

Benzalacetone-4-methylthiosemicarbazone is obtained as yellow needles from dilute alcohol. It melts at 149°. It is freely soluble in benzene, chloroform, pyridine, glacial acetic acid and alcohol but insoluble in ligroin. (Found: S, 13·46. $C_{11}H_{15}N_3S$ requires S, 13·73 per cent.).

Benzalacetone-4-a-naphthylthiosemicarbazone comes out from dilute alcohol in yellow crystals which melt at 189°. It is easily soluble in benzene, chloroform, carbon disulphide and pyridine but moderately in alcohol and glacial acetic acid. (Found: N, 12·23. $C_{21}H_{19}N_3S$ requires N, 12·17 per cent.).

A General Method for the Preparation of Thiosemicarbazones in Alcohol.

Condensations could also be successfully effected in alcoholic solution. About two hours' time was necessary to have complete reaction. The following thiosemicarbazones were prepared using alcohol.

Cinnamylidene-thiosemicarbazone crystallises out in pale yellow needles (m.p. 134-135°) from glacial acetic acid. (Found: S, 15·2. $C_{10}H_{11}N_3S$ requires S, 15·6 per cent.).

Cinnamylidene-4-o-tolylthiosemicarbazone comes out as colourless crystals from alcohol. It melts at 207°. It is moderately soluble in alcohol, pyridine, chloroform and benzene. (Found: N, 14·3. $C_{17}H_{17}N_3S$ requires N, 14·2 per cent.).

Benzalacetone-4-o-tolylthiosemicarbazone crystallises from alcohol in yellow needles melting at 185°. It is highly soluble in benzene, chloroform, carbon disulphide and glacial acetic acid but moderately in alcohol. (Found: N, 13·65. $C_{18}H_{19}N_3S$ requires N, 13·59 per cent.).

Benzalacetone-4-phenylthiosemicarbazone.

Molecular proportions of benzalacetone and 4-phenylthiosemicarbazide were heated in pyridine solution for half an hour. The solution was allowed to cool and concentrated. The separated crystals were freed from the mother-liquor and crystallised from

glacial acetic acid in brown needles melting at 163-164°. (Found : N, 14·55. $C_{17}H_{17}N_3S$ requires N, 14·23 per cent.).

It is fairly soluble in benzene, chloroform, pyridine, alcohol but moderately in glacial acetic acid.

Condensation of Cinnamic Aldehyde with Benzyldithiocarbazinate.

Benzyldithiocarbazinate (1·9 g.) was dissolved in hot anhydrous alcohol, cinnamic aldehyde (1·3 g.) added and the mixture heated on the water-bath for 10 minutes.   On cooling the condensation product separated out.   This was freed from the mother-liquor and crystallised from pyridine when pale yellow needles melting at 183° were obtained. (Found : N, 9·2. $C_{17}H_{16}N_3S_2$ requires N, 8·97 per cent.).

It is moderately soluble in alcohol, pyridine and glacial acetic acid but insoluble in ligroin.

Condensation of Benzalacetone with Benzyldithiocarbazinate.

Molecular proportions of benzalacetone and benzyldithiocarbazinate in anhydrous alcohol were heated on the water-bath for about two hours.   The solution, on concentration, deposited red crystals.   These were recrystallised from benzene with the addition of ligroin in colourless crystals which turned red on coming in contact with air.   It melts at 130-131°.   (Found : N, 8·65. $C_{18}H_{18}N_2S_2$ requires N, 8·58 per cent.).

The compound is soluble in most organic media but insoluble in ligroin.

Our sincere thanks are due to Sir P. C. Rāy who has taken a keen interest in the investigation.

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On the Variability of Valency.

By Sir Prafulla Chandra Ráy, Kt., C.I.E., D.Sc., Ph.D.,

President, Indian Chemical Society.

The conception of valency has undergone many changes since it was first formulated by Berzelius. The idea of constant valency derived from the behaviour of carbon compounds and so strongly upheld by Kekulé and others had to ultimately give way to that of variable valency, as serious difficulties were encountered in representing the formulæ of inorganic compounds. Valency may now be regarded as a variable function of several factors. These latter may be summed up as follows:

(1) The valency of an atom varies according to the nature of the combining atoms. The nitrogen behaves as mono-, di-, tri-tetra-, and penta-valent towards oxygen but only trivalent towards chlorine. Sulphur is hexavalent towards oxygen and fluorine as in SO_3 and SF_6; but its maximum valency towards chlorine is only four as given by SCl_4. Manganese is heptavalent in its highest oxide Mn_2O_7 but becomes tetravalent in its highest chloride. Iron is di- and tri-valent towards chlorine but is hexavalent towards oxygen.

(2) The valency of an element also depends upon external conditions.

(a) Thus valency often varies with temperature,—generally decreasing with increasing temperature. Dissociation of PCl_5, CO_2, SO_3, I_2, S_2 etc. furnishes instances of the kind.

(b) Pressure also exerts a similar influence retarding the dissociation of many compounds with a higher valency of the central atom into those of a lower valency.

(c) Medium also plays an important rôle in certain cases. Thus some compounds can exist only in solution or in the solid state. For example compounds like HI_3, HBr_3, $HCII_2$, $HClBr_2$ and $HBrI_2$, are known in solution only; and $KICl_2$, NH_4ICl_2, $KIBr_2$ and NH_4IBr_2 are known only in the solid state.

(d) Presence or absence of certain substances in the medium can also determine the condition of valency. Thus the tetravalent oxygen of H_2O_2 becomes unstable in aqueous solution containing hydroxyl ions, whereas hydrogen ions increase its stability. Attention might also be drawn in this connection to the influence of minute traces of water vapour in bringing about or retarding

many commonplace reactions as has been so ably demonstrated by Prof. Baker.

(e) Relative concentration of the reacting atoms also affects the combining capacity of the central atoms. Chlorine in excess acting upon phosphorus forms PCl_5 whereas phosphorus in excess acting upon chlorine generates PCl_3.

A consideration of all these facts led to the doctrine of variable valency which formulates that it is not an inherent property of the atom as such but depends upon the nature of the atoms with which it combines and also upon external physical conditions.

Further changes in this fundamental conception of valency were introduced later on to explain many new important properties of substances as they were gradually discovered. One of the most striking contributions in this direction was made by Alfred Werner— the father of co-ordination chemistry. The theory was advanced by him to elucidate the constitution of the so-called molecular or complex compounds which presented serious difficulties to the application of the existing theories of valency. After many unsuccessful efforts made by Blomstrand. Jörgensen and others. it was left to Werner to bring law and order into this chaotic region of complex compounds. The success which this theory has attained is too well-known to be elaborated here. One of the fundamental assumptions of the co-ordination theory is that the central combining atom possesses a maximum co-ordination value of 4, 6 or 8 according as it is di-, tri- or tetra-valent. The atom always tends to satisfy the maximum co-ordination value. But as in the case of simple or primary valencies, maximum co-ordination or complex valency also changes according to the nature of the co-ordinated atoms, groups or radicles and is further influenced by external physical conditions. A host of compounds can be named in which the co-ordination number is one, two, three, five, seven. eight and even more than that, though these compounds are not so stable as the cobalt and platinum compounds with sixfold co-ordination. Some typical examples of these are given here.

Co-ordination value one : $AgX.NH_3$; $AuCl.NH_3$.

Twofold co-ordination : $AgX\cdot 2NH_3$; $CuCl\cdot Me_2S$; $CuCl\cdot CH_3CN$; $AuCl\cdot Me_2S$.

$AgNO_3\cdot C_6H_4(CN)_2$; $CuBr.P(OCH_3)_3$;

$AgCN.KCN$; $AgSCN.KSCN$; $AuCl.KCl$;

$KF.HF$; $(C_6H_5)_3ICl$; $CuCN.KCN$.

Threefold co-ordination: $CuX.3NH_3$; $CuCl.3Py$; $AuCl.3NH_3$;
$[Cu.[CS(NH_2)_2]_3]X$; $CuCl_2.3Py$;
$HgCl_2. Et_2S.$
$PtCl_2.CO$; $PtCl_2.PCl_3$; $2KCN.NiCN$;
$CuCl_2.KCl$; $HgI_2.KI$; $(CH_3)_3SX$;
$(C_6H_5)_3C.Cl.$

Fivefold co-ordination : $\begin{bmatrix} Pt(NH_3)_4 \\ (C_6H^6NH_2)_3 \end{bmatrix}\overset{II}{S}O_4$; $CuSO_4.5NH_3$;
$CdCl_2.5NH_3$; $SnCl_4.(C_2H_5)_2O.$

Sevenfold co-ordination : $LiI. 7NH_3$; $SiF_4. 3NH_4F$;
$SbCl_5. 2HCl$; $BiI_3.4KI.$

Eightfold co-ordination : $Mo(CN)_4. 4MeCN$; $W(CN)_4. 4MeCN$;
$[Cu(NH_3)_2]Pt(CNS)_4.$

From what has been said above it can now be concluded that valency is not an invariable characteristic of an element as its atomic weight is; nay, even the latter, after the discovery of isotopes by Aston has ceased to be a constant. Hence both the normal and co-ordination valencies of an atom may change with changing circumstances. An elementary atom which usually exhibits di and tetra-valency may under special conditions become tri-, penta-, and hexa-valent as well. I shall deal here with two special cases only, that of platinum and gold.

The platinum atom, as is well known, generally gives compounds of the types PtX_2 and PtX_4 in which platinum is di- and tetra-valent respectively. Compounds of different types have also been described in the literature. The following oxides and chlorides of the metal have been described : PtO, Pt_2O_3, PtO, PtO_2, $PtCl$, $PtCl_2$, $PtCl_3$ and $PtCl_4$. These clearly indicate that the platinum atom can manifest mono-, di-, tri-, tetra- and hexa-valency.

Gold is also usually regarded as mono- and tri-valent but it also acts as divalent as in the compounds AuO (gold dioxide) and $AuSO_4$ (auroso-auric sulphate).

It has already been shown with respect to mercaptanic radicles and organic sulphides that platinum exhibits all different valencies up to a maximum of eight.

With dithio-ethylene glycol $C_2H_4(SH)_2$, platinic chloride reacts according to the following scheme giving compounds of ter-, quadri-,

quinque-, sexa- and octa-valent platinum according to the conditions of the experiment.

$$x\text{HS·CH}_2\text{·CH}_2\text{SK} + \text{PtCl}_4 \longrightarrow \text{Pt(SC}_2\text{H}_4\text{SH}), \text{ where } x = 3,4, \ 5, \ 6, \text{ or } 8.$$
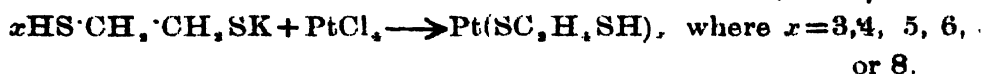
The nature of the compounds obtained greatly depends upon the temperature of the reaction. With increasing temperature compounds of decreasing valency of platinum are obtained. This is in line with the general observation already made that rise of temperature tends to lower the valence of an elementary atom. Further it should also be noticed that in no case the valency of platinum has been found to exceed eight as is required by its position in the periodic table.

Now turning to the complex compounds of platinum obtained by the action of chloroplatinic acid upon ethyl sulphide under different experimental conditions, a similar observation regarding the co-ordination valency of platinum can be made. The compounds obtained may be tabulated as below :

(a) $\text{PtCl.Et}_2\text{S.}$
(b) $\text{PtCl}_2\text{.2Et}_2\text{S.}$
(c) $\text{PtCl}_3\text{.2Et}_2\text{S.}$
(d) $\text{PtCl}_4\text{.2Et}_2\text{S.}$
(e) $\text{PtCl}_5\text{.2Et}_2\text{S.2H}_2\text{O.}$

Some of these compounds under (b) and (d) have already been described by Blomstrand, Tschugaeff and Malschewsky. The compound (b) has been isolated in six different isomeric modifications. Of these two have already been described by Blomstrand and are known as cis-trans isomers.

Compound (a) may be regarded to exhibit a co-ordination value of two only Of the six isomers of the compound (b) in which the co-ordination value is evidently four, constitution of the three can be accounted for in the following way :

(1) Blomstrand's cis-compound.
(2) Blomstrand's trans-compound.
(3) $[\overset{\text{II}}{\text{Pt}}(\overset{\text{II}}{\text{Et}_2}\text{S})_4]\text{PtCl}_4$

Compound (c) can be represented as molecular compound of (b) and (d). $[\ (\overset{\text{II}}{\text{Et}_2}\text{S})_2\text{.PtCl}_2\ ][\ (\overset{\text{IV}}{\text{Et}_2}\text{S})_2\text{PtCl}_4\ ]$ or $[\ \overset{\text{II}}{\text{Pt}}(\overset{\text{II}}{\text{Et}_2}\text{S})_4\ ]\overset{\text{IV}}{\text{PtCl}_6}.$

The former is preferred as, on crystallization from alcohol, it breaks up into the two constituent molecules. This is further confirmed by the action of ammonia upon it, which gives an ammonical complex $\left[\overset{II}{Pt} (NH_3)_4 \right] Cl_2$.

Compound (c) can be constituted as $H_2 \left[Pt \overset{Cl_3}{OH} \right].(Et_2S)_2.H_2O$ showing a higher co-ordination value than six.

Compound (a) PtCl.Et$_2$S cannot be adequately represented by Werner's theory and it must be assumed that the co-ordination value of the monovalent platinum atom is two. By the action of bases like ethylamine, benzylamine, pyridine and piperidine it gives compounds of the type, PtCl$_2$, 4B; Pt$_2$Cl,B,Et$_2$S; PtCl$_2$,2B; 2Pt Cl,4B,Et$_2$S.

The compound (c) PtCl$_4$,2Et$_2$S, 2H$_2$O, by the action of bases, gives compounds of the type PtCl$_4$,2B and PtCl$_4$,2B.

Similar compounds have also been obtained from platinic chloride and benzyl sulphide.

What has been stated regarding the valency of platinum applies equally well to the case of gold. As is well-known gold usually forms compounds of the mono- and tri-valent type and only in rare cases of the divalent type. But with respect to mercaptanic radicles it resembles platinum forming compounds in which it behaves as a bi-, ter-, quadri-, and quinque-valent atom. Diethyl disulphide and auric chloride have been found to give a crystalline compound of the composition 2AuCl$_3$.Et$_2$S$_2$, the gold apparently behaving as divalent and a white amorphous powder having the composition Au$_4$Cl$_2$.Et$_2$S$_2$.

By the action of auric chloride upon the monopotassium salt of dithio-ethylene glycol, a compound of the composition Au$_2$Cl.(C$_2$H$_4$S$_2$)$_2$ has been obtained. This can be represented constitutionally either as

$$\overset{II}{Au}<\overset{S.C_2H_4.S}{S.C_2H_4.S}>AuCl, \text{ or, } \overset{III}{\underset{CH_2-S}{CH_2-S}}>\overset{IV}{Au}<\overset{S-CH_2}{S-CH_2} AuCl.$$
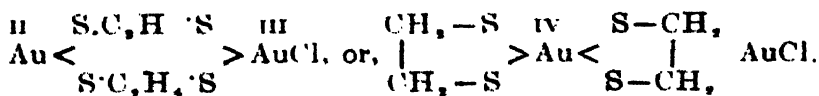
In the first case one atom of gold acting in bi- and the other atom in ter-valent condition. In the second case it is regarded as a molecular compound of aurous chloride with quadrivalent auric thioglycollate.

Benzaldiethylene tetrasulphide with auric chloride yields the compound,

$$Au_3Cl_4.\ 2C_6H_5{\cdot}CH < \begin{matrix} S-C_2H_4-S \\ S-C_2H_4-S \end{matrix} \Big|$$
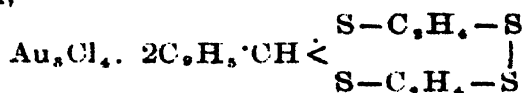
which may be represented as a molecular compound·like

$$2AuCl.AuCl_2.2C_6H_5{\cdot}CH < \begin{matrix} S-C_2H_4-S \\ S-C_2H_4-S \end{matrix} \Big|$$
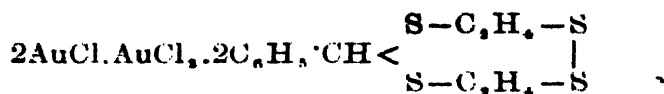
the gold functioning as mono- and bi-valent. When, however, benzaldiethylene trisulphide is similarly treated, the molecule is broken up and compounds of diethylene disulphide are obtained, thus :

$$C_6H_5.CH < \begin{matrix} S-C_2H_4 \\ S-C_2H_4 \end{matrix} > S \ \dashrightarrow \ S < \begin{matrix} C_2H_4 \\ C_2H_4 \end{matrix} > S$$
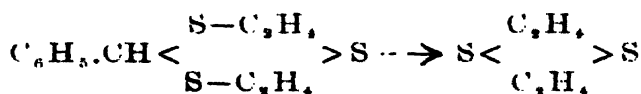
<div align="right">1 : 4-Dithian.</div>

The following compounds have thus been obtained :—

(a) $6A.Au_2Cl_3$

(b) $5A.Au_3Cl_5$

(c) $4A.Au_3Cl_4$

(d) $4A.Au_3Cl_2$.

(e) $3A.Au_3Cl_2$

(f) $3A.Au_2Cl_3$ where $A = 1 : 4$-dithian.

It is very difficult to explain the anomalous nature of these chlorides according to our usual conception of the valency of gold.

Compound (a) can only be represented as a sulphonium compound in which the gold behaves as bi- and ter-valent respectively.

Compound (b) and (c) can be regarded as molecular compounds like $5A, 2AuCl, AuCl_3$; $4A, 2AuCl, AuCl_2$. Compounds (d) and (e) should be regarded as sulphonium compounds like (a), and (f) as a molecular compound of $2AuCl.3A$.

Triethylene trisulphide with auric chloride on the other hand gives two compounds, namely, $2AuCl_3.\ (C_2H_4S)_3$ and $(C_2H_4S)_3$, $AuCl_3$. These can of course be represented as simple molecular compounds of tervalent and bivalent gold respectively. Or, we may consider them as sulphonium compounds with quinquevalent and quadrivalent gold respectively.

By the interaction of sodium dithioethylene glycol and auric

chloride in acetone solution a quinquevalent gold compound of the formula

$$\left[\begin{array}{c} CH_2-S \\ | \\ CH_2-S \end{array} > \right]_3 Au_2$$
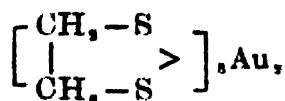
has been obtained. When the reaction occurs in ethereal solution, the compound $Au_2Cl.(C_2H_4S_2)_4$ is obtained, the gold retaining its tervalency intact.

The action of bases like ammonia and pyridine upon some of these gold compounds has been studied. In almost all the cases the final products consist of molecular compounds of monovalent gold, AuCl.

By the action of ammonia upon Au_2Cl_2. $(C_2H_4)_2S_2$ a compound of the composition Au_2Cl_2. $6NH_3$ has been obtained which cannot be accounted for by the usually accepted valencies of gold.

It can thus be concluded that valency is variable, and it is significant that two of the most noble metals platinum and gold exhibit the greatest possible variation in this respect.'

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Preparation of 4-Acetylamino-3-Chlorophenyl Stibinate of Sodium.

By Sudhir Chandra Niyogy.

The compound to be described in this communication is known in trade as "Von Heyden's 471" but no details as to its method of preparation or properties seem to have been published by Heyden. Recently Brahmachari and Das (*J. of Indian Medical Research*, **13**, 17) have prepared this compound by the chlorination of *p*-acetyl-amino-phenyl stibinate of sodium with sodium hypochlorite.

The method of preparation described in this paper is entirely different. (1) The starting material is not acetyl *p*-phenylenediamine but 4-acetylamino-3-chloroaniline. (2) Von Heyden's method (*Fabr. Heyden*, D. R. P. 254421) for the introduction of an antimony complex into the aromatic nucleus is a tedious process and unsatisfactory as regards the yield (which is of the greatest importance in this case). Percy May (*J. Chem. Soc.*, 1912, **10**i, 1037) has shown that diazonium chlorides form additive compounds with antimony trichloride solution, which are only very sparingly soluble in ordinary solvents. These when decomposed with sodium hydroxide solution give off the diazo nitrogen and the antimony complex goes into the nucleus.

EXPERIMENTAL.

4-Acetylamino-3-chloro-aniline (4 g.) was dissolved in hydro-chloric acid (5 c.c.) and water (15 c.c.). This solution was cooled in ice and diazotised. After the diazotisation, hydrochloric acid (5 c.c.) was added. Antimony trichloride solution, prepared by dissolving antimony trioxide (4 g.) in hydrochloric acid (15 c.c.), was added slowly to the solution of the diazonium salt, with stirring. A crystalline precipitate immediately separated. The whole was then kept in ice for one hour and then filtered at the pump. The preci-pitate was washed twice with hydrochloric acid (*d* 1·12) to remove antimony trichloride and then with water till free from acid.

The mass was beaten up with water (60 c.c.). Sodium hydroxide

(6 g.) in water (20 c.c.) was added gradually with vigorous stirring. Rapid evolution of nitrogen was noticed and the stirring was continued till it had appreciably slackened, and the whole was allowed to stand overnight. The liquid was then filtered and the residue twice extracted with small quantities of boiling water. The combined filtrate was acidified with dilute sulphuric acid when the free acid separated as a light flocculent precipitate. This was washed thoroughly with water to remove inorganic impurities and then beaten up with a small quantity of water. This emulsion was slightly warmed on the water-bath and sodium hydroxide solution added drop by drop till the whole had gone into solution. The solution was concentrated on the water-bath and absolute alcohol was added in excess when the sodium salt of 4-acetylamino-3-chlorophenyl stibinic acid separated. This was collected, washed with absolute alcohol to remove alkali and dried in a vacuum desiccator.

The course of the reaction may be shown thus :
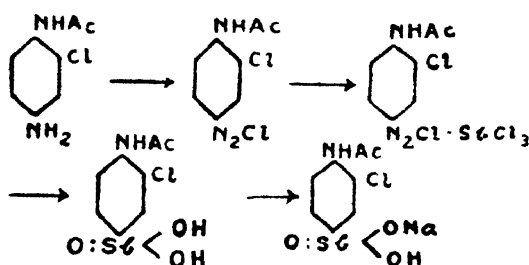
Properties. A light brown amorphous powder, soluble in water, the solution being neutral to litmus. It does not give the diazo reaction. (Found: N, 3·3 ; Sb, 32·8. $C_8H_8O_4NClSbNa$ requires N, 3·8 ; Sb, 33·3 per cent.).

My thanks are due to Prof. H. K. Sen for the kind interest he has taken in the course of this work without which it would have been difficult for me to finish it.

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13

A Theory of Colour on the Basis of Molecular Strain. Part II.

A General Exposition of the Theory.

By Sikhibhushan Dutt.

The first part of this investigation has already been published (*J. Chem. Soc.*, 1926, **129**, 1171). The present work is only an extension of the latter with a view to a general exposition of the theory.

On systematic investigation of the whole series of organic compounds it is found that the unsaturated groups may be arranged in the following order of increasing absorptive power:—

C : C, C ⦂ C, C : O, C : N, C ⦂ N, C : S, N : N, N : O.

In an union between any two of these atoms by double linkage, the valency directions tend to straighten out and coalesce or form a pair of parallel lines under the opposing forces of repulsion:

$$\text{>}\!C\!\text{<} \ + \ \text{>}\!C\!\text{<} \ \rightarrow \ \text{>}\!C\!\diamondsuit C\!\text{<} \ \rightarrow \ \text{>}\!C = C\!\text{<}$$
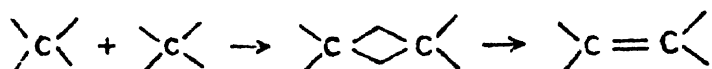
Under such conditions the total angle distorted between each of the following pairs of atoms from theoretical considerations is as follows:—

1.	C : C	..	...	...	$109 \cdot 5° + 109 \cdot 5° = 219°$
2.	C : N	.	...	...	$109 \cdot 5 + 120 = 229° \cdot 5$
3.	C : O	..	...	...	$109 \cdot 5 + 180 = 289° \cdot 5$
4.	N : N	..	...	...	$120 + 120 = 240°$
5.	N : O	..	...	...	$120 + 180 = 300°$

The only anomalous case in the above table from the point of absorption is that of the carbon-oxygen double bond, because from theoretical considerations it should be a much more strained system than the nitrogen-nitrogen double bond, but from considerations

of its absorptive power (for absorption maximum) it is found tu be a less strained system than even the carbon-nitrogen double bond. This fact must have a direct bearing on the remarkable stability of carbon monoxide and dioxide, which from their chemical and physical properties seem to indicate that there are practically very little strains in the systems. It is also a very significant fact that carbon has got the strongest affinity for oxygen which it will abstract from any oxygenated compound under suitable conditions. So it appears that the actual angle distorted in an union of carbon and oxygen by double bond is not $289 \cdot 5°$ as given in the above table, but considerably less, because for want of repulsive force between the atoms, the actual valency directions will not be straightened out into parallel lines, but will maintain a considerable degree of curvature (as in a magnetic field) in a stable union, thereby retaining the greater portion of the angle between the two consecutive valencies of each atom in an undistorted state. Thus :—
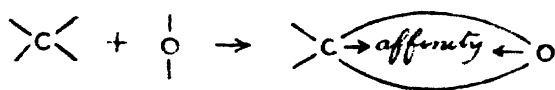
There is also another fact which may be brought to bear on this point, and that is the quadrivalency of oxygen, which is well known in most of the pyran derivatives, and also in many heterocyclic compounds containing oxygen in the ring. Under such circumstances where oxygen behaves as a quadrivalent element, its actual valency directions may be supposed to be nearly the same as those of carbon, so that by the union of carbon and oxygen by double bond, the actual strain produced is the same as in a carbon to carbon double bond. In cases where oxygen behaves as an apparently divalent but potentially quadrivalent element, this strain becomes a little greater, because the angle between its two active valency directions must necessarily be greater than that between the two latent ones. And since practically in every case where oxygen is known to behave as a quadrivalent element, it never exerts its latent valencies unless under somewhat forcible circumstances, so it will be clear that in a carbon-oxygen double bond the actual strain is a little greater than in a carbon-carbon double bond. Similar is the case where an oxygen atom joins one or more systems with formation of a pyran like derivative. There the actual strain becomes a little greater than in the corresponding

homocyclic derivative containing carbon* in place of oxygen. Thus :—

| Xanthene 2970 | Dihydro- anthracene 2700 | Diphenylene oxide 3030 | Fluorene 2935 |

| Coumarane 2830 | Indene 2770 | Butyrolactone 2600 | cyclo Pentanone 2730 |
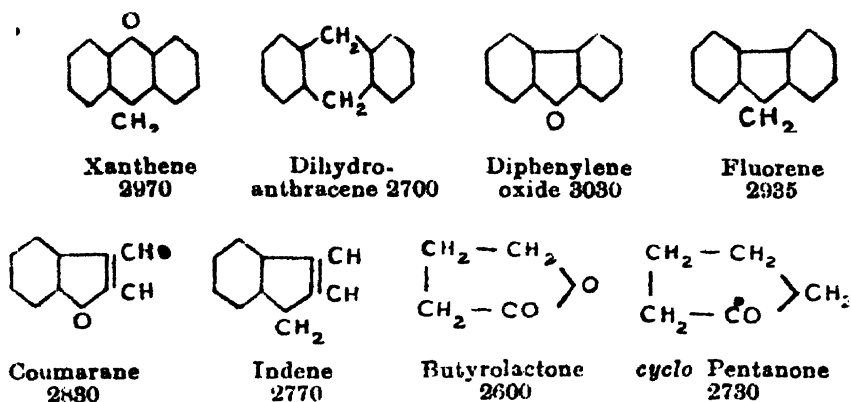
The fact that C:O in a ketonic or aldehydic compound has got a greater absorption than that in the carboxyl may be accounted for by the assumption that there is a difference of configuration and therefore of strain in the two systems. While ketonic or aldehydic C:O contains a true bivalent oxygen as is shown by the formation of the dichloride by phosphorus pentachloride, the carboxylic C:O contains the atom in a quadrivalent state, so that the structure of the carboxyl may be represented by the following :—
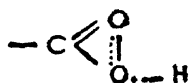
This explanation will account for the greater reactivity of the carboxylic hydrogen as compared with the alcoholic hydrogen, because in the former case the hydrogen is attached to a quadrivalent oxygen by one of its auxiliary valencies, while in the latter case the hydrogen is attached to the bivalent oxygen by one of its normal valencies.

Amongst the five systems of double bonds, the nitrogen-oxygen double bond is the most highly strained system of all. That is clearly manifest in the remarkable instability of these compounds. They often decompose spontaneously or on the slightest provocation, and are very readily attacked by oxidising or reducing agents. On account of high strain in the molecule the nitroso compounds are well marked by their great absorptive power. Thus:—

Nitrosobenzene	...	7300	ter-Nitrosobutane ... 6390
p-Nitrosotoluene	...	7300	ter-Nitrosoisopropylacetone ... 6600
Nitrosomesitylene	...	7320	

But if the nitroso group is in a molecule containing a labile hydrogen atom, it automatically rearranges itself to a condition of less strain in the following manner:—N : O—⟶ =N.OH. For example in nitrosophenol and nitrosodimethylaniline, the automatic rearrangement of the nitroso groups becomes like this :—
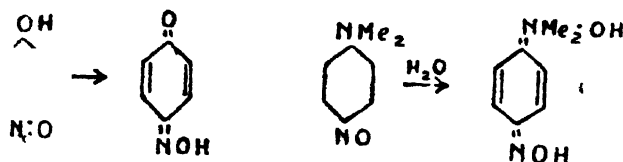
Many of the nitroso compounds tend to lose their internal strain by the formation of bimolecular ring compounds, thus :

$$2\text{-N} : \text{O} \longrightarrow \begin{array}{c} \text{-N---O} \\ | \quad | \\ \text{O---N-} \end{array}$$
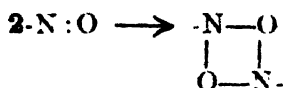
It is a well known fact that the nitroso compounds in their bimolecular forms are colourless, while the monomolecular forms are marked by their intense colour.

From the chemical point of view the amount of tension in a double bond between two atoms is determined by the following considerations :—

(1) The amount of negative affinity or repellant force between the atoms.

(2) The stability of the molecule containing the double bond to physical forces of light, heat, electricity, &c.

(3) The ease with which the molecule is attacked by chemical agents at the double bond.

For the first two facts there is at present no means of definite measurement. An attempt was therefore made to measure the third factor in the following manner :—

Equimolecular quantities ($\frac{1}{10}$ mol.) of five substances containing the double bonds,— C : C, C : N, C : O, N : N, and N : O, e.g., stilbene, benzylidene-aniline, benzophenone, azobenzene and nitrosobenzene were dissolved in the same volume (200 c.c.) of absolute alcohol, the same quantity of colloidal palladium added to each and then the solutions contained in air-tight bottles were connected to a reservoir of pure hydrogen and under pressure and shaken at frequent intervals for three hours. At the end of that time the loss of volume

of hydrogen due to absorption was carefully measured in each case. From the data thus obtained and also from analyses of the resultant products as far as possible, it was found that the substances were reduced to the following extent :—

1. Nitrosobenzene 100%
2. Azobenzene 65%
3. Benzylideneaniline 35%
4. Benzophenone 27%
5. Stilbene 7%

In the above instances hydrogen was chosen as the reacting chemical agent, because it is the only agent capable of attacking all the above five substances. Though the results obtained are not claimed to be very accurate, yet they show plainly enough, that from the point of view of internal strain, the double bonded systems may be arranged in the following increasing order of magnitude :—C :C, C :O, C :N, N :N, N :O. These results are in close agreement with those obtained from a study of absorption spectra of compounds containing these double bonds.

Now in order to find a relation between molecular strain and absorption of light, colourless substances having no strain in the molecule may be supposed to respond under the influence of light to vibrations of all frequencies in such a manner that there is little loss of energy. In other words a strain-free molecule may be supposed to be an elastic and almost frictionless system which transmits vibratory energy practically without any absorption. The natural frequency of resonance of such a system under the influence of a periodic force such as light is not expected to be of any definite character. but in all possibility it will resonate with vibrations of very high frequency mainly, and with forced vibrations of lower frequencies to a less extent. So that the molecule under such circumstances will have a slight, more or less general absorption over the whole range of the spectrum specially in the infra-red, owing to the greater energy carried by the latter vibrations, and a selective absorption at high frequency in a region which lies far into the ultra-violet beyond the range of the quartz spectrograph. This is supported by the fact that absorption bands in the shorter wavelengths have increasingly sharp and narrow boundaries, while the boundaries towards the infra-red tend to become progressively wide and indistinct, thus showing that with increase of wave-length and

hence increase of energy content, forced vibrations of the molecule become more prevalent, while with shorter vibrations and consequent less energy content, the major absorption is due to rosonance.*

By the entrance of a double bond, that is a region of strain in the molecule, a certain amounnt of frictional force is brought into play, so that the molecule now begins to absorb a certain amount of energy on account of the damping effect of friction on vibration. Consequently the system now resonates with vibrations of lower frequency, and the selective absorption of the molecule is brought into the ultra-violet region of the spectrum. As the strain in the molecule increases, the frictional force also increases, so that the molecule can only resonate with vibrations of diminishing frequency containing increasing amount of energy. Hence the selective absorption of the molecule gradually shifts towards the red end of the spectrum.

The strain and consequent friction may be regarded as the potential energy of a system containing a double bond, which in many cases is gradually expended in counteracting the physical force of light. It is a well known fact that the vast majority of dyestuffs get bleached under the influence of strong sunlight sooner or later. From the heat of combustion of unsaturated substances it has also been established that they contain more potential energy than corresponding substances without unsaturation.

Colour and the chemistry of coloured substances have invariably been linked with the constitution of the benzene nucleus. From the amount of work that has been done on the subject, it appears that there are three double bonds in the molecule, of a modified character, not giving under ordinary conditions the reactions of olefinic linkage. In all probability the double bonds are in a constant state of oscillations and rearrangement through the various phases of Kekule's, Bayer's and Dewar's formulæ (cf. Ingold, J. Chem. Soc., 1923, **123**, 2066; also 1922, **121**, 1133, 1143). Under such circumstances the benzene nucleus presents a spatial character of want of static strain, which otherwise could be expected from a cyclic structure containing three fixed double bonds. On account of this peculiar character, the actual strain in the benzene nucleus

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* Bands are obtained instead of lines which would be expected of resonance, because the strain though mainly remaining constant, may vary within narrow limits, on account of different positions which groups joined by single bonds may take in space by free rotation around the bonds.

becomes less than that in another system of six carbon atoms containing three fixed double bonds as in hexa-triene. For while benzene has an absorption maximum at about λ2500, hexa-triene has an absorption at about λ2600. It is also a significant fact pointing to the same conclusion that hexa-triene is attacked by chemical reagents with far greater rapidity than benzene.

When the internal strains of benzene assume a more static form as in the formation of a quinonoid or similar structure, the total strain in the molecule becomes much greater than when the strains were in an exceedingly labile dynamic form. That is the reason why the quinonoid forms of benzene show more colour development than the corresponding non-quinonoid forms. That is also a reason why dyes that are quinonoid in all possible tautomeric forms are more coloured than those which have an intermediate non-quinonoid form (cf. Watson J. Chem. Soc., 1914, **105**, 760). The fulvenes are more coloured than benzenes, because unlike the latter the internal strains in them are of perfectly static nature, and hence more powerful than in the benzenes. This is also shown by the greater reactivity of the fulvenes as compared with the benzenes.

The theory of chromophores and auxochromes as propounded by Witt and others is nothing but a vague and indefinite statement of a general phenomenon. A chromophore is really an organic molecule containing one or more seats of tension of various characters, while an auxochrome is a group or radical which essentially facilitates a static re-arrangement of the internal strains of the benzene nucleus under suitable conditions. It is in reality a vulnerable point in the benzene nucleus which by the action of various chemical reagents helps in the fixation of the strained structure.

The number of ways in which the internal strains of benzene nucleus may be arranged in a static form is large, but the following may be given as a few typical examples :—
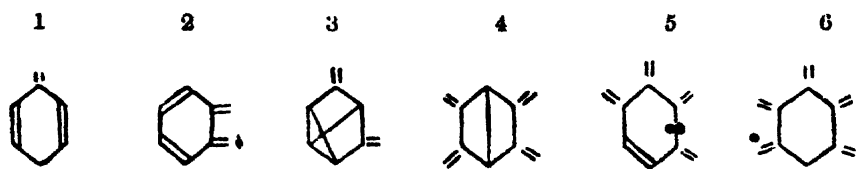
The first is the well known *para*-quinonoid structure. The second is the equally well known *ortho*-quinonoid structure. A

comparison between the two structures from the spatial point of view will show that No. 2 is the more strained system of the two because of the existence in it of unbalanced tension, and also that while No. 1 has one degree of freedom. No. 2 has none at all. This will account for the fact that *ortho*-quinonoid structures always show more colour than the corresponding *para*-quinonoid structures.

Structure No. 3 should be the *meta*-quinonoid structure. The existence of such a structure has been denied by many chemists, but there is no reason whatever that it should not be capable of formation, though it is much less likely than the other two structures. The violet colour of quino-phthalein in alkali can easily be explained by the assumption of such a structure as Meyer has shown. The same may be said of the constitution of tetraphenyl-*m*-xylene prepared by **Stark** and **Garben** (*Ber.*, 1913, **46**, 659).

Structures No. 4, 5, 6 etc. are also known in the poly-quinoyl derivatives of benzene, *e.g.*, nitranilic acid, rhodizonic acid, etc. It is also possible to assume their existence in the poly-hydroxy derivatives of anthraquinone when they are dissolved in alkali, whereby greater strain is introduced into the systems and the colours are also greatly intensified. Thus :—
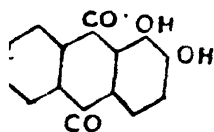
Alizarine in alcohol
4390
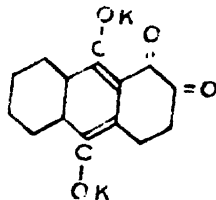
Alizarine in KOH
5730
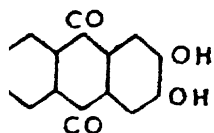
2 :3-Dihydroxy-anthraquinone
in alcohol 4480
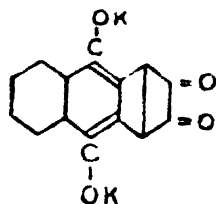
2 :3-Dihydroxy-anthraquinone in
KOH 6080

In a system that is under strain, the effect of a load is to increase the strain provided it acts within close proximity of the strain.

The further away the load is from the position of the strain, the less will be the effect. Interesting examples of this phenomenon will be found in the fluorescein series in which the effect of substituents on the two benzene nuclei bearing the two hydroxy groups will be to produce an increase of strain on the pyrone oxygen linking which is already in a condition of strain (*vide supra*). Hence a substituent will be most efficient if it is nearest to the oxygen atom. The further away it is from the atom the less will be the effect. Thus :—
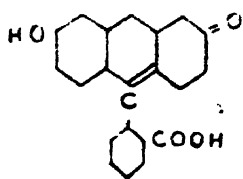
Fluorescein
1910
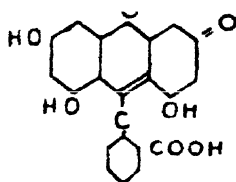
Phloroglucinol-
phthalein, 4980
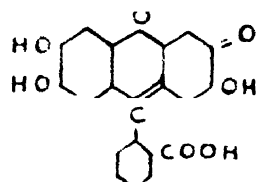
Hydroxyquinol-
phthalein, 5540
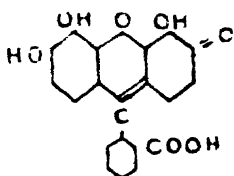
Gallein 5980

Similar is the case with pyranol dyes containing a pyrone oxygen atom. Thus (Watson, "Colour in Relation to Chemical Constitution" p. 105) :—
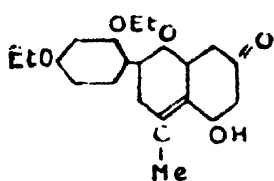
5550
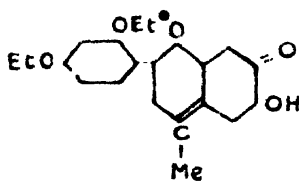
5730
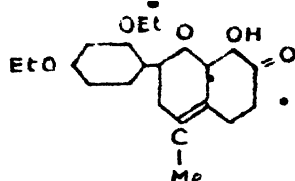
6120

When an open-chain compound is converted into a ring compound, there is generally produced an increase of strain due to distortion of the normal valency directions of the atoms, and

consequently the total strain of the molecule is also greatly increased. Thus :—

n-Butyl-benzene	... 2580	Benzil	...	4080
Tetrahydro-naphthalene	... 2740	Phenanthraquinone	...	4440
Benzophenone	... 3000	Diphenylamine	...	2980
Fluorenone	... 3610	Carbazole	...	3080
Diphenyl-methane	... 2570	Diphenyl-butadien	...	3100
Fluorene	... 2935	Benzal-indene	...	3730
α-Ethyl-naphthalene	... 2780	Glyoxanilide	...	3650
Acenaphthene	... 2890	Isatin	...	4120
Stilbene	... 2860	Tetraphenyl-ethylene	...	3210
Phenanthrene	... 2930	Bis-fluorene	...	5270

When two sources of strain in a molecule are in juxtaposition to one another, either acting on a common atom or separated by only one single linkage, the total effect of the strains will be greater than in the case where the strains are separated by some distance. The reason lies in the fact that when an atom has two of its valency directions in a double bond, the remaining valency directions though singly linked are in a somewhat strained condition due to the distortive effect produced on them by the double bond. Thus :—

Name.	Formula.		Absorption maxima.
Acetone	... $CH_3.C:O.CH_3$	...	2630
Diacetyl	... $CH_3.C:O.C:O.CH_3$	...	4100
Triketopentane	... $CH_3.C:O.C:O.C:O.CH_3$	...	4830
Acetylacetone	... $CH_3.C:O.CH_2.C:O.CH_3$	...	2730
Acetonyl-acetone	... $CH_3.C:O.CH_2.CH_2.C:O.CH_3$		2730
Benzophenone	... $C_6H_5.C:O.C_6H_5$	...	3000
Benzil	... $C_6H_5.C:O.C:O.C_6H_5$	...	4160
Diphenyl-triketone	$C_6H_5.C:O.C:O.C:O.C_6H_5$	...	4950
Benzoyl acetophenone	$C_6H_5.C:O.CH_2.C:O.C_6H_5$	...	3130

A somewhat similar thing also happens if one of the benzene nuclei in a fused ring system is hydrogenated so as to remove its internal strain. Thus :—

Naphthalene ...	2760	Benzene-azo-4-naphthol	4990
Tetrahydro-naphthalene...	2740	Benzene-azo-tetrahydro-4-naphthol	4150
Anthracene ...	2950	Carbazole ...	3030
Dihydro-anthracene (9 : 10)	2700	Tetrahydro-carbazole ...	2780

Similar is the reason why substances with conjugated systems of double linkages are always more absorptive than substances with non-conjugated systems of double linkages, that is with double linkages widely separated (cf. Crymble, Stewart, Wright and Glendining. *J. Chem. Soc.*, 1911, **99**, 451; Crymble, Stewart, Wright and Rea, *ibid*, p. 1202). That is also the reason why reduplication or superposition of chromophores with widely separated seats of strain does not produce the desired increase of colour (Dutt, *J. Chem. Soc.*, 1926, **129**, 1171).

When two sources of strain act on the same atom, the effect is still more intensified. Thus :—

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} > C:HCC:O.CH_3$$

Mesityl oxide, 2910

$$\begin{matrix} C_2H_5 \\ \\ C_2H_5 \end{matrix} > C:C:O$$

Diethyl ketene, 3950

$$C_6H_5CH:CH \cdot C:O \cdot CH_3$$

Cinnamone, 2970

$$\begin{matrix} C_6H_5 \\ \\ C_6H_5 \end{matrix} > C:C:O$$
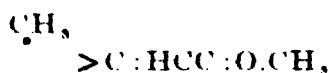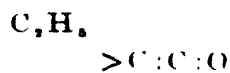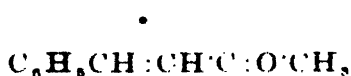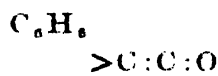
Diphenyl ketene, 4980

The greater portion of the spectroscopic work has been carried out in the laboratory of Prof. A. Fowler of the Imperial College. London, to whom my best thanks are due.

EDWIN ROY WATSON

Born July, 1880; Died November, 1926

Edwin Roy Watson.

Born July, 1880; Died November, 1926.

BY BAWA KARTAR SINGH.

Edwin Roy Watson, second son of William Watson and Emily Watson (née Bond) was educated at the Nottingham High School, where he held scholarships throughout his school career. He went up to Jesus College, Cambridge, in 1899 with the senior entrance scholarship. He obtained high Honours in the first part of the Natural Sciences Tripos in 1901 and in the second part in 1902. He spent two years (1902-04) in post-graduate research in chemistry at Cambridge under the guidance of Dr. S. Ruhemann. He came out to India in 1904 as Professor of Chemistry at the Sibpur Engineering College, Bengal. After about two years' work there, he was transferred to Dacca College, Dacca, in a similar capacity where he worked till 1921. He was then transferred to Cawnpore as Principal of the newly established Government Technological Institute. He was overworked during the latter part of his service and consequently suffered from a nervous breakdown, which necessitated his taking leave out of India last April. He consulted some nerve specialists in Switzerland, but finding no relief there, he returned to London. He did not recover from mental depression, and died in November 1926, under circumstances of peculiar sadness, at the early age of forty six.

Watson took a very prominent part in the development of higher chemical teaching in this country, and the object of this note is to describe some of his contributions to chemical science. Besides being a very able and attractive lecturer in chemistry, he prosecuted research very vigorously both himself and with the help of his advanced students.

Watson published three papers in 1904 at Cambridge, two of them jointly with Dr. Ruhemann and the third independently. The first of these papers (*J. Chem. Soc.*, 1904, **85**, 456) dealt with the preparation of ketones of the acetylene series with a view to see whether they are transformed by the action of bases into heterocyclic compounds similar to those formed from the esters of the acetylene series (Ruhemann and Stapleton, *J. Chem. Soc.*, 1900, **77**, 239).

In the second paper (*J. Chem, Soc.*, 1904, **85**, 1170) it was shown that unsaturated olefinic ketonic compounds form addition

products with organic bases and that these additive compounds which are first formed, subsequently undergo further changes.

In the third paper (*J. Chem. Soc.*, 1904, **85**, 1319) Watson showed that the action of bases on acetylenic ketones is to form additive compounds by the addition of the base to the carbon atoms of the acetylenic linking. This behaviour is analogous to the addition of bases to olefinic ketonic compounds. This research had also as its object the preparation of acetylenic ketones.

On his arrival in India, Watson made a break with the above type of research, and started on an entirely new line. He studied (*J. Chem. Soc.*, 1906, **89**, 578) the electrolysis of silver nitrate by altering the current-concentration and density and also the strength of the solution. He found that the anodic product in all cases was silver peroxynitrate Ag_7NO_{11}. The decomposition of this compound with boiling water was shown to take place according to the following equation :

$$Ag_7NO_{11} = AgNO_3 + 3Ag_2O_2 + O_2$$

One of the products of this decomposition was silver dioxide which was claimed to have been obtained pure for the first time.

From 1909 to 1922 Watson published about thirty papers, either alone or in collaboration with his pupils, on the chemistry of dyes. It will be thus seen that he again returned to organic chemistry, but cultivated an entirely different subject from that with which he was associated at Cambridge. In this respect he proves himself to be at once original and very resourceful.

His earlier studies in this branch related to testing the fastness of dyes of the polyhydroxy-benzophenone series (*J. Soc. Chem. Ind.*, 1911, **30**, 196). He established that an increase in the number of hydroxyl groups tends to diminish the fastness to light, with the exception of the 2 : 3 : 4-trihydroxy compound. Most of these dyes are brightened and deepened by treatment with alkali, and the xanthones are not so fast to acid or light as the polyhydroxybenzophenones. This subject was further studied in a later paper (*J. Chem. Soc.*, 1912, **101**, 1238).

In another communication (*J. Soc. Chem. Ind.*, 1911, **30**, 6, it was shown that benzene-azo-salicylic acid, when dyed with a chrome mordant, is characterized by a fastness towards light, alkali and acid superior to that of any other simple mono-azo dye. Attempts to prepare similar dyes (*ibid*, 1912, **31**, 968) having the same all round fastness, but of a deeper colour, by replacing the phenyl

group with heavier hydrocarbon residues, or with other groups containing chromophores, and also by substituting a-hydroxynaphthoic acid residue for that of salicylic acid, met with only partial success.

Since many azo-dyes of not more complicated structure possess the desired shades, a number of well-known azo-dyes prepared from naphthol sulphonic acids were examined (*ibid*, 1913, **32**, 642), from which it was concluded that the relative position of the hydroxyl- and chromophore groups is the determining factor in the colour of the dye, the ortho-position favouring red, violet, and blue shades, and the para-position giving brown shades.

In 1912-13, Watson's attention was drawn to the insect *Cydnus Indicus* (*J. Chem. Soc.*, 1913, **103**, 548). At Dacca this insect is attracted to lights, often in large number in the nights of June and the following rainy months. It is notorious on account of its strong and unpleasant odour. It is known in Bengali as *gandi*. It is also known as *geranium-bug* and belongs to the *Heteroptera*. Maxwell-Lefroy ("Indian Insect Life") remarks that "a feature of the great majority of Heteroptera is the aromatic odour they protect themselves with. This odour is due to the secretion by special glands of an oily fluid, which is excreted at will from the odoriferous orifices and rapidly volatilises." Watson found that the strong and disagreeable odour of *Cydnus Indicus* is due to cycloheptane carboxylic acid which is present in the insects to the extent of $1\frac{1}{2}$ per cent., and another substance ($C_{11}H_{20}O_2$?) present in much smaller quantity (0·1—0·2 per cent.). The intensity of the odour of the latter substance can be judged from the fact that each insect contains 0·000005 gram of it, and yet one insect is sufficient to scent the whole room.

Watson's interest in dye-chemistry was not confined only to the production of dyes of tinctorial value. He put forward a very remarkable theory on the relation between chemical constitution and depth of colour of dyes (*J. Chem. Soc.*, 1914, **105**, 759). According to this theory those dyes which are quinonoid in all possible tautomeric forms exhibit a deep colour, however simple the molecule may be. On the other hand, if there is the possibility of the molecule existing in a non-quinonoid form, it may not attain a deep colour, although the molecular complexity may be very considerable. A survey of all the better known dyestuffs fully bears out this theory, and it explains remarkable differences in depths of colour between dyes of very similar constitution. A permanent

quinonoid structure alone is not sufficient, for example dihydroxy-p-benzoquinone ; the substance must be capable of tautomerising from one quinonoid arrangement to another. The theory has been fully borne out by the preparation of dyes of deep colour from quercetin (see below).

The quest for the ultimate cause of colour has led to the production of a great mass of literature on the theoretical side of the subject by a number of chemists. Its scientific interest and its practical utility led Watson to throw himself enthusiastically into this line of research. In 1917 Watson gave a course of lectures on " Colour and Constitution" at the University of Leeds. These lectures were published in the following year in the series of Monographs on Industrial Chemistry edited by Sir Edward Thorpe (Longmans Green & Co.) and show the great mastery of the subject possessed by Watson.

During the years 1911-15, Watson was engaged in the study of dyes of the flavone group. In the first paper of the series (*J. Chem. Soc.*, 1914, **105**, 338) experiments were described which had as their object the introduction of an additional hydroxyl group into the quercetin molecule. By the methods employed, however, this could not be effected, because it was found impossible to convert amino-quercetin pentamethyl ether by means of the diazo-compound into the corresponding hydroxy-derivative. On the other hand, amino-quercetin was successfully prepared and it was shown that the amino group exerted but little effect on the tinctorial property of the dye.

With the same object in view, namely, to deepen the colour of the dye and to prepare new polyhydroxy flavones which might prove of future service in the study of the natural members of the group, identical methods were applied to both luteolin and morin (Perkin and Watson, *J. Chem. Soc.*, 1915, **107**, 198). Luteolin and morin after being converted into their ethers were nitrated and the nitro groups reduced to amino groups. As in the case of the analogous quercetin compound, attempts to displace the amino group by hydroxyl in amino-morin-pentamethyl ether failed. The influence of the new auxochromes was studied spectroscopically, and it was found that a multiplication of auxochromic groups resulted in a widening of the principal absorption band, and a slight shift in its position towards the red end of the spectrum. The effect on the second band which lies in the violet and ultraviolet was apparent in the spectroscope, but alteration in this band had little influence on the visible colour of the substance. It was established that

whereas an increase of auxochromes deepens the colour very considerably in certain groups of dyes, as is shown in the difference between alizarine, and alizarine blue W. R., and fluorescein and gallein, in other cases, such as flavone group, a similar multiplication of auxochromes has very little effect on the colour.

The foregoing methods having failed to produce deeper-coloured dyes, various other attempts were carried out (*J. Chem. Soc.*, 1914, **105**, 389 ; 1915, **170**, 1477). 6'-Nitroquercetin pentamethyl ether was partly demethylated, yielding 6'-nitroquercetin dimethyl ether but this was found to be useless for dying purposes. Various attempts to introduce additional auxochromes failed, and the multiplication of chromophoric groups in the molecule also gave rise to unsatisfactory results. Success was obtained in another way. The objective sought was to introduce into the molecule some substituent which would produce a permanent quinonoid structure, and this was gained by replacing the pyrone ketonic radicle by the group— CR·OH. The new compounds of this type might be expected to resemble in behaviour the dyes of the triphenyl carbinol series. Compounds of the following structure (I and II) were, therefore, prepared by the action of Grignard's reagent on quercetin pentaethyl ether and subsequent de-ethylation with hydriodic acid. The base corresponding with II dyes wool violet or crimson, according as to whether alum or tin is used.
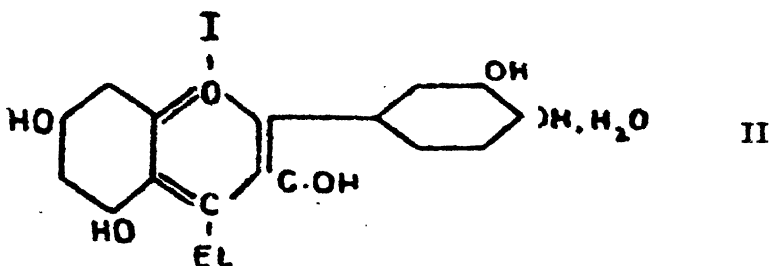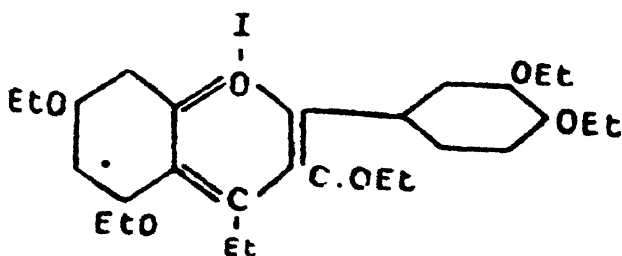
* This series of compounds possesses considerable interest in connection with the colour of flowers, fruits, etc. Willstätter's work

(Willstätter and Mallison, *Sitzungsber. K. Akad. Wiss.*, Berlin, 1914, 769) has shown that these natural colouring matters are very closely related to the compounds obtained by Watson and his pupils and possess very similar properties.

Other studies by Watson related to the preparation of dyes from phenanthraquinone (*J. Soc. Chem. Ind.*, 1915, **34**, 1136 ; *J. Chem. Soc.*, 1921, **119**, 1211) and of sulphide dyes (*J. Chem. Soc.*, 1920, **117**, 830 ; 1922, **121**, 1939, 2414).

In 1921, Watson was selected as Principal of the newly established Technological Institute at Cawnpore by the Government of the United Provinces. Watson threw himself, with his usual enthusiasm, into the organisation of this new Institute. He took a very considerable part in teaching and carried out a good deal of research work in technological subjects, some of which is published in the Journal of our Society. He was forced to abandon his chemical studies on dyes on account of the nature of his new duties—a circumstance which he much regretted. This divorce from his former scientific studies was keenly felt by him and coupled with his heavy duties at Cawnpore hastened his tragic and premature death. At Dacca also he worked very hard and spent about ten hours daily in the laboratory and trained a band of students in research, who are now serving as successful teachers of chemistry in different parts of the country. His simple and straightforward manner greatly endeared him to his students and colleagues.

Watson received the degree of Doctor of Science of the University of London in 1913. He was President of the Chemistry Section of the Indian Science Congress held at Bangalore in 1924 and gave a very illuminating and interesting address on the organisation, direction and stimulation of chemical research (*Proc. Eleventh Ind. Sci. Congress*, 1924, 68). He was a Vice-President of the Indian Chemical Society, the inception of which owes much to him.

Watson married Lily Mary Hurtston, of Leamington Spa at St. George's Cathedral, Madras, in October, 1908, and had two children who died in infancy. One of his brothers, Harold Argyll Watson, of the Indian Civil Service, is at present serving in the Madras Presidency. Watson's main recreation was painting and he had exhibited with success at Simla, Naini Tal, and other fine arts exhibitions.

His death is a very great loss to our Society in particular and to Chemical Science in general. He leaves numerous friends both in this country and in England to mourn his loss.

Peptisation of Metallic Hydroxides in Presence of Sugars.

By M. R. MEHROTRA AND K. C. SEN.

It is well known that in presence of some non-electrolytes like glycerol and sugars, the precipitation of many metallic hydroxides by the addition of caustic alkali to the salt solutions is often prevented. The nature of the substances formed in solution was however in doubt for many years. Graham (*J. Chem. Soc.*, 1862, **15**, 253) considered that sucrates of copper and iron were present in the clear liquid when caustic alkali was added to a solution of copper or iron salt in presence of cane sugar. Until recently quantitative experiments in this line were wanting though many qualitative observations have been made (*Cf.* Bancroft, IInd B. A. *Report on Colloid Chemistry*, p. 2). In a previous paper one of the present authors (Sen and Dhar, *Kolloid Zeit.*, 1923, **33**, 193) has studied the peptisation of various hydroxides in presence of some non-electrolytes in a semi-quantitative way. Recently Kuhn and Pirsch (*Kolloid Zeit.*, 1925, **36**, 310, and Zsigmondy Festschr) in Wo. Ostwald's laboratory have made a detailed study of the peptisation of bismuth hydroxide in presence of several sugars in the same way as Sen had previously done. As the subject is an interesting one and seems to have an important bearing on the general theory of peptisation, it was considered desirable to undertake some more quantitative work in this connection. The peptisation of copper, mercury, iron and cerium hydroxides has been studied in presence of sucrose, dextrose, laevulose and lactose in various concentrations, and an account of these experiments is given in this paper.

EXPERIMENTAL.

Semi-normal solutions of the chlorides of the metals (except that of mercury which was one third normal) were prepared. The standard solution of mercuric chloride was prepared by weighing out the required quantity of the salt; those of copper, cerium and ferric chloride were made by diluting strong standard

solutions in which copper was standardised against thiosulphate, and iron and cerium were estimated gravimetrically. Solutions of sugars (Kahlbaum's pure chemicals) were also prepared by weighing. The solutions were all molar except that of milk sugar which was usually semimolar. A seminormal caustic soda, free from carbonate as much as possible, was prepared to form the hydroxides of the metals. The amount of alkali added was always in excess of that required to form completely the hydroxide of the metal. The minimum amount of any sugar necessary to prevent the formation of a visible precipitate was found out as follows.

A known volume of the salt solution under investigation was measured out from a pipette graduated into a hundredth of a c.c. and mixed with varying amounts of sugar solutions in test tubes. In other test tubes a definite amount of alkali was diluted with calcu-lated amounts of distilled water in order to make the combined mixture salt plus sugar plus alkali 15 c.c. The solution of caustic soda was then mixed with the salt solution. From the results to be presented later on, it was early observed that the total volume in which the peptisation is allowed to take place and the quantity of caustic soda used for forming the hydroxide affect the amount of sugar necessary to prevent the formation of a visible precipitate. It was therefore necessary to keep the volume constant at 15 c.c. in all the experiments, and the amount of alkali added was also kept constant. In all cases except that of iron, the solution re-mained clear on the addition of the mixture of water and alkali to the mixture of salt and sugar, if the requisite amount of sugar was present. But with ferric hydroxide it was observed that a solution which was at first turbid cleared up if the shaking was continued for some time. Consequently in the experiments with iron, the shaking was continued for five minutes in every case and the amount of sugar recorded in the tables against each quantity of iron is the minimum quantity necessary for the solution to become clear after five minutes of shaking. The results obtained are tabulated below in Tables I, II, III and IV.

TABLE I.

Peptisation of Copper Hydroxide.

Vol. =15 c.c.; NaOH=3 millimoles.

Copper chloride (in millimoles).	Amount of sugar necessary to prevent precipitation (in millimoles).			
	Sucrose	Dextrose	Laevulose	Lactose
0·1	...	...	...	0·0175
0·125	...	0·035	0·025	...
0·20	...	...	...	0·085
0·25	0·10	0·07	0·06	0·0475
0·35	...	...	0·11	0·075
0·375	0·19	0·095	...	...
0·45	...	...	...	0·11
0·50	0·25	0·15	0·20	0·135
0·60	...	...	0·25	0·19
0·625	0·31	0·28	...	...
0·70	...	0·36	...	0·24
0·75	0·64	0·45	0·35	0·275
0·85	...	...	0·45	...
0·875	1·05	...	...	...
0·95	...	...	0·37	...
1·0	2·7	...	0·60	>2·5
1·125	>4·5	...	...	..

TABLE II.

Peptisation of Ferric Hydroxide.

Vol. =15 c.c.; NaOH=3 millimoles.

Amount of FeCl₃ (millimoles).	Amount of sugar necessary to prevent precipitation (in millimoles).			
	Sucrose.	Dextrose.	Laevulose.	Lactose.
0·0334	...	0·165	...	...
0·0668	0·31	...	0·045	0·15
0·0835	0·37	0·29	...	...
0·1336	...	...	0·09	0·205
0·167	0·55	0·46	0·10	0·325
0·2338	...	...	0·15	0·485
0·2505	0·77	0·65	...	...
0·3006	...	...	0·20	0·64
0·334	1·05	0·98	0·25	0·70
0·4008	...	...	0·40	1·30
0·4175	1·55	1·58	...	...
0·4675	...	...	0·565	1·925
0·501	2·1	2·0	0·64	2·40

TABLE III.

Peptisation of Mercuric Oxide.

Vol. =15 c.c.; NaOH =3 millimoles.

Amount of HgCl$_2$ (millimoles).	Amount of sugar necessary to prevent precipitation (in millimoles).			
	Sucrose.	Dextrose.	Lævulose.	Lactose.
0·0333	0·19	0·40	0·17	0·17
0·0666	0·58	1·0	0·39	0·55
0·09996	0·99	1·65	0·61	0·96
0·1333	1·5	2·15	0·82	1·2
0·1666	2·1	2·85	1·2	1·45
0·1999	2·9	3·5	1·45	1·7
0·2332	3·7	4·0	1·75	2·05
0·2666	4·6	4·55	1·95	2·35
0·2999	5·65	5·3	2·3	...
0·3332	6·5	5·8	2·55	...
0·4165	...	...	3·25	...
0·4998	...	...	3·95	...

TABLE IV.

Peptisation of Cerium Hydroxide.

Vol. =15 c.c.; NaOH=3 millimoles.

Amount of CeCl$_3$ (millimoles).	Amount of sugar necessary to prevent precipitation (millimoles).			
	Sucrose	Dextrose	Lævulose	Lactose
0·0166	...	1·0	...	...
0·0332	...	2·0	0·19	0·22
0·0498	..	3·05	...	..
0·0664	0·17	4·2	0·53	0·44
0·0830	...	>6·5		...
0·0996		...	1·1	0·65
0·1328	0·32	...	1·6	0·88
0·166	0·38	...	1·9	1·10
0·1826	...	..	...	1·22
0·1992	...		3·0	
0·2324	0·56		3·7	1·565
0·2656	..		4·8	
0·2822	...		...	1·875
0·2988	0·73		5·7	...
0·3320	0·77	...	>7·0	2·25
0·3984	0·90	...	..	...
0·4648	1·08	...	...	..
0·4980	1·20	...	..	...
0·564·	1·90	...	..	...
0·6308	2·56	...	...	...
0·6640	2·90	..		

Non-electrolyg fe sucrose

Mannit

Glucose

Glycerin

(Urea?)

Amount of salts in millimoles.

Amount of sugar in millimoles.

60

50

40

30

20

10

The curves have been drawn in a slightly different way, the ordinate being the concentration of one particular sugar whilst the abscissa represents the concentration of different salts. It is believed that the specific effect of sugars in the peptisation of different hydroxides will be better observed in this way. For purposes of illustration only one series of curves is given.

Discussion.

A glance at the curves given in Fig. I shows that in many cases the relation between the amount of hydroxide peptised and the amount of sugar necessary to prevent precipitation is a simple one, for in the cases of mercury and cerium (with three out of four sugars) the curves are straight lines. In the case of copper too, the earlier portion of the curve at low concentrations of the salt is almost a straight line. Consequently these curves can be represented by an equation of the type $C_s = A \cdot C_m + B$, where C_s is the amount of sugar in millimoles; C_m is the amount of metallic hydroxide in millimoles, and A and B are constants for the particular experiment. In the following table the values of A and B, and the limit within which the equation holds, are shown for various sugars.

TABLE V.

Sugar.	A	B	Metal	Limits of salt concentration within which the equation is applicable. (in millimoles)
Dextrose	68·5	−0·95	Cerium	0·0166 to 0·0664
	18·4	−0·90	Mercury	0·0433 to 0·3332
	2·2	+0·10	Iron	0·0334 to 0·2506
	0·28	0·0	Copper	0·125 to 0·5
Sucrose	0·68	−0·075	Copper	0·25 to 0·625
	2·40	0·0	Cerium	0·0664 to 0·498
	2·50	+0·145	Iron	0·0666 to 0·2505
Lactose	6·8	−0·02	Cerium	0·0332 to 0·332
	0·21	−0·005	Copper	0·10 to 0·35
	2·1	+0·005	Iron	0·0668 to 0·334
	2·87	−0·0025	Mercury	0·0833 to 0·2666
Laevulose	0·404	−0·033	Copper	0·125 to 0·35
	8·33	−0·16	Mercury	0·0333 to 0·4998
	2·646	0·0	Iron	0·045 to 0·3006

It will be observed from this table that the values of B are often negative, and in several cases, notably with copper and dextrose, with cerium and sucrose, with iron and lævulose and practically with copper and iron and lactose, the values of B are zero. In other words, in these particular cases, the equation reduces to $C_s = A.C_m$, i.e., the amount of hydroxide peptised is directly proportional to the amount of sugar present within the limits of salt concentration given in the table.

It will be recalled that Graham called these peptised solutions of copper and iron as sucrates of copper and iron. As a matter of fact up to the concentrations in which, $C_m/C_s =$ constant, we might indeed conceive that a really definite compound is formed. As soon as however one goes out of this particular concentration range, the relation $C_m/C_s =$ constant no longer holds, and therefore the probability of a definite chemical compound formation with a constant ratio of C_m/C_s breaks down. From Table V it will be observed that out of 14 cases, only 5 experiments can be represented by an equation of the type $C_m/C_s = k$. Since there is no reason to believe that the other experiments are absolutely different in nature from these five, it is obvious that in these five cases, the results are only accidental. To consider, however, this point of the probability of a compound formation more fully, the molecular ratio of metal to sugar has been calculated in the cases of copper and iron, and are given in the following tables.

TABLE VI.

Amount of iron (milli gr. atom) peptised.	Ratio of gr. atom iron to gr. mole sugar in the peptised stа			
	Sucrose.	Dextrose.	Lævulose.	Lactose.
0·0668	0·22	...	1·48	0·45
0·1670	0·30	0·36	1·67	0·51
0·3340	0·32	0·34	1·33	0·48
0·5010	0·21	0·25	0·78	0·21

TABLE VII.

Amount of Cu in milli gr. atom peptised.	Ratio gr. atom Cu to gr. mole sugar in the peptised state.			
	Sucrose.	Dextrose.	Lævulose.	Lactose.
0·25	2·5	3·57	4·16	5·26
0·50	2·0	3·33	2·5	3·70
0·625	1·84	2·23	...	...
0·75	1·17	1·66	2·14	2·6
1·00	0·37	...	0·33	<0·4

These results show that the ratio of metal atom to sugar is very variable and depends upon the actual amount of hydroxide peptised. From Table VII it appears that there is a gradual fall in the value of the ratio with increase in the actual amount of the peptised hydroxide, but with iron in Table VI no such relation is observable, for the ratio at first rises and reaching a maximum, decreases. It appears therefore that no simple relation exists between the two. The specific nature of sugars in the peptisation of hydroxides is also obvious from these tables, namely the variation in the values of this ratio with different sugars. From the curves it has been observed that the peptisability of the different hydroxides is in the same order in the case of dextrose and lævulose, namely, $Cu>Fe>Hg$ $>Ce$, but in the case of sucrose the order is $Cu>Ce>Fe>Hg$ and in that of lactose, it is $Cu>Fe>Ce>Hg$. This is of course the order when the results are expressed in moles, but will vary when the results are expressed in equivalents. It is curious also that the actual amount necessary to peptise a definite amount of hydroxide should be so very different in the case of dextrose and lævulose, and sucrose and lactose. This fact alone goes against the hypothesis of any definite chemical compound formation. In the following pages it will be shown that the actual volume of the solution in which the experiment is made, and the amount of alkali used have also a great effect on the amount of sugar necessary to peptise a definite amount of hydroxide.

Effect of Volume.

The experiments so far discussed were all done in a constant volume of 15 c.c. It was thought desirable at this time to make some experiments with different total volumes, to see whether any variation in the actual amount of sugar necessary to peptise a definite amount of hydroxide occurs or not. In the following two tables the results with copper and mercury are shown at two other volumes, 10 c.c. and 7 c.c. with sucrose only. The amount of alkali remains the same, namely 3 millimoles. For the sake of comparison, the ratio of metal to sugar is shown at all the volumes.

TABLE VIII.

Amount of Cu (milli gr. atom) peptised.	Millimoles of sucrose.		Ratio Cu Sugar		
	Vol. = 10 c.c.	Vol. = 7 c.c.	Vol. = 7 c.c.	Vol. = 10 c.c.	Vol. = 15 c.c.
0·125	0·05	0·05	2·5	2·5	...
0·25	0·11	0·115	2·17	2·28	2·5
0·375	0·195	0·20	1·87	1·92	..
0·50	0·265	0·32	1·56	1·68	2·01
0·625	0·40	0·47	1·33	1·56	1·84
0·75	0·90	1·00	0·75	0·83	1·17

TABLE IX.

Amount of Hg (milli gr. atom) peptised.	Millimoles of sucrose.		Ratio Hg Sugar.		
	Vol. = 10 c.c.	Vol. = 7 c.c.	Vol. = 7 c.c.	Vol. = 10 c.c.	Vol. = 15 c.c.
0·0333	0·3	0·34	0·098	0·111	0·175
0·0666	0·69	0·82	0·081	0·096	0·115
0·0999	1·2	1·45	0·068	0·083	0·101
0·1333	1·7	2·35	0·056	0·075	0·038
0·1666	2·35	>3	<0·055	0·071	0·079

It will be apparent from Tables VIII and IX that the volume of the solution has no appreciable effect when the amount of metal ion is very small, but at moderate concentrations of the salts, the volume in which peptisation is studied has a decided effect on the amount of sugar necessary to peptise the hydroxide. Thus it will be observed, in both the tables, that the ratio of metal to sugar gradually increases, as the volume of the solution increases. In other words, less of sugar is necessary to peptise a definite amount of copper and mercury hydroxide at higher volumes than that required to peptise at lower volumes. It is difficult to give a satisfactory explanation of this phenomenon, but it appears that for each volume of solution and amount of sugar, there is a maximum amount of colloid which can be retained by the system.

Effect of Amount of Alkali.

It has already been mentioned that the amount of sugar necessary to prevent precipitation of a certain quantity of any hydroxide depends upon the actual amount of alkali present in the system. A further study of the phenomenon was, therefore, made with mercuric chloride and copper chloride in presence of sucrose. The results are given below in Tables X and XI. The total volume was 15 c.c.

TABLE X.

Amount of copper (milli gr. atom) peptised.	Millimoles of sucrose.		
	NaOH = 2 milli-moles.	NaOH = 3 milli-moles.	NaOH = 5 milli-moles.
0·125	0·05	—	0·04
0·250	0·14	0·10	0·10
0·375	0·20	0·19	0·175
0·500	0·31	0·25	0·23
0·625	0·85	0·34	0·32
0·750	>8·0	0·64	0·55

TABLE XI.

Amount of Hg (milli gr. atom) peptised.	Millimoles of sucrose.		
	NaOH = 1·5 milli-moles.	NaOH = 3 milli-moles.	NaOH = 5 milli-moles.
0·0333	0·19	0·19	0-25
0·0666	0·42	0·58	0·62
0·0999	0·81	0·99	1·05
0·1333	1·20	1·50	1·58
0·1666	1·70	2·10	2·20
0·3332	5·7	6·50	—

From these tables it will be observed that the influence of the change in the amount of alkali is not appreciable at lower concen, trations of the salts studied, specially copper. In the case of mercury, however, when only 1·5 millimoles of alkali are present, the difference in the values of sucrose necessary to prevent precipitation from those required when 3 millimoles of alkali are present becomes obvious even at low concentrations. This remarkable difference is probably due to the coagulating effect of caustic soda on mercuric oxide at higher concentrations of the alkali. A similar effect may account for the higher values of sucrose when the total volume is less than 15 c.c. in the case of mercury. The behaviour of copper, however, does not seem to fit in with such an explanation. The results in the case of smaller volumes are quite intelligible on the explanation put forward above. But the values of sucrose found to be sufficient to check precipitation of copper hydroxide when larger quantities of alkali are used appear to contradict this suggestion. According to this view, one would expect higher amounts of sugar to be necessary when 5 millimoles of alkali are used than when only 3 millimoles are present. But on the contrary, the amount found is actually less than that in the case of 3 millimoles of alkali. In other words, with greater amounts of alkali there is a peptising action noticeable. Attention may also be drawn to another interesting point. From Table X it may be observed that even 8 milli-moles of sucrose failed to prevent the formation of a visible precipitate from 0·75 milligram atom of copper when 2 millimoles of

alkali are used, but when 3 millimoles of alkali are present, 0·64 millimoles of sucrose are quite efficient to check the formation of a visible precipitate. This shows that to prevent by means of a sugar the appearance of a precipitate of a metallic hydroxide, it is not sufficient that a certain amount of alkali be present in excess than is required to form the hydroxide of the metal, but it is essential that a certain minimum excess of alkali be present.

Time Effect on Peptisation.

As already stated in the case of iron, there appears to be a time factor in the phenomenon of peptisation. In the case of copper as well, it was noticed that at higher concentrations of the salt the peptisation was not immediate, but it required shaking for a minute or two. The solution became clear even if the test tube was set aside for a while. In both the cases of iron and copper, shaking probably helps in the mechanical disintegration of the precipitate. In the case of mercury the reverse phenomenon occurred. It was noticed in the experiments that although the solutions remained clear on the addition of alkali to the mixture of salt and the requisite amount of sugar, a precipitate of mercuric oxide appeared on standing for some time, unless there was great excess of sugar. With increasing amount of sugar, the time of appearance of the precipitate also increased.

Summary and Conclusion.

(1) An experimental study has been made of the peptisation of the hydroxides of copper, iron, mercury and cerium in presence of sucrose, dextrose, laevulose and lactose in various concentrations.

(2) The effect of sugars is a specific one and there is a marked difference between sucrose and lactose, and dextrose and laevulose in the power of preventing the precipitation of hydroxides.

(3) With dextrose and laevulose, the order of peptisation of different chlorides comes in the series Cu > Fe > Hg > Ce, but with sucrose the series is Cu > Ce > Fe > Hg, and with lactose Cu > Fe > Ce > Hg.

(4) The volume of the solution and the amount of alkali used have great effects on the minimum amount of sugars necessary to prevent precipitation of hydroxides. It is always necessary to have

a minimum excess of alkali present.   In some cases, turbid mixtures become clear on standing, but in the case of mercury, the reverse may happen.

(5) In the case of several experiments it was found that the amount of hydroxide peptised was directly proportional to the amount of sugar present, but this is not general. The ratio of metal to sugar is variable depending upon the amount of the hydroxide peptised, the volume of the solution and the amount of alkali present, and hence there is no possibility of a definite chemical compound formation between the hydroxide and the sugar.

In conclusion, a few remarks may be made as to the probable way in which the sugar and alkali afford the protection which has been observed.   It is generally admitted that the peptisation is usually preceded by adsorption of the protecting substance by the substance peptised.   Bancroft (*J. Phys. Chem.*, 1916, **20**, 85) has suggested that peptisation in general is brought about as a result of the lowering of the surface tension of the adsorbing material on account of the adsorbed substance and consequently believes that peptisation may result as a sequel of the adsorption of even non-electrolytes or undissociated salt molecules. In a recent paper one of us has discussed the theory of peptisation in detail. (Sen, *J. Phys. Chem.*, 1925, **29**, 1533) There is no question that sugars are adsorbed by the hydroxides and the mechanism of sugar adsorption by several colloids has been considered by some authors (Bhatnagar and collaborators, *J. Phys. Chem.*, 1924, **20**, 730 ; 1925, **19**, 166) to be chemical in nature.   This fact of the adsorption of sugar alone, however, does not explain the mechanism of the peptisation of the hydroxides.   Thus it has been shown in this paper that the peptisation of the hydroxides observed is clearly affected by the amount of alkali employed. Not only is the amount of sugar necessary to prevent the formation of a visible precipitate controlled by the change in the quantity of alkali present but a certain minimum excess of alkali is necessary before any amount of sugar added can check the formation of a visible precipitate.   This clearly indicaties that the part of the alkali in bringing about the peptisation of the hydroxides is of great importance.   It is probable that in presence of excess of alkali, the adsorption of sugar may be decreased, and hence greater amounts of sugars would be necessary to prevent precipitation of the hydroxides.   As already stated, the results with copper, however, point to the exactly opposite conclusion.   Hence the effect of alkali cannot be explained by simply connecting it with its

probable influence on the adsorption of sugar by the hydroxide particles.

It will be interesting to note here that these peptised solutions are only stable in presence of an excess of acid or alkali. Thus ferric hydroxide is stable both in acid and alkaline medium whereas copper hydroxide is peptised when the solution is alkaline. When alkali is added gradually to a mixture of ferric chloride and sugar, there is no formation of a precipitate but at the same time no test of free alkali is obtainable in the solution. What happens is that at first a positively charged colloid is formed. Owing to the presence of undecomposed ferric chloride, the stability is quite high, but with the gradual addition of alkali, the charge diminishes and the colloid ultimately coagulates. If the hydroxyl ion concentration is still more increased, the coagulum dissolves forming a negatively charged sol. This coagulation and stabilisation into either positively or negatively charged sol can be brought about as many times as desired by simply adding suitable quantities of either acid or alkali. Since this is so, the question arises, what is the function of sugar in this case of peptisation? That the non-electrolyte has some action is evident from the fact that we do not get usually a negatively charged ferric hydroxide with caustic soda unless precautions are observed (Cf. Powis, J. Chem. Soc., 1915, **107**, 818). On the other hand sugar does not stabilise the colloid in the absence of a minimum excess of H or OH' ions.

We are consequently of opinion that in the cases studied in this paper where excess of alkali has always been used, the observed peptisation is the combined result of the presence of both alkali and sugars, and in any interpretation of the mechanism of the inhibition of the precipitation of metallic hydroxides in presence of sugars, the effect of the excess of alkali has also to be considered as at least of equal if not of more importance than the sugars. (See, in this connection, Sen, J. Phys. Chem., 1925, **29**, 1546).

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Peptisation of Iron and Chromium Hydroxides in Presence of Non-electrolytes and the Influence of Acid and Alkali on the Peptisation.

By Kshitish Chandra Sen.

In a recent paper on the peptisation of metallic hydroxides in presence of non-electrolytes (Mehrotra and Sen, this *volume*, p. 115) it has been shown that though the effect of different non-electrolytes is specific and in some cases depends upon both the non-electrolyte and the metallic hydroxide peptised, yet there is one similarity in every case, namely that a little excess of alkali always favours peptisation. It was also stated that the peptised solution of ferric hydroxide is stable in both acid and alkaline solutions whereas copper hydroxide can only be obtained as a blue solution in presence of excess of alkali. In this paper it has been shown that a minimum excess of acid or alkali is necessary before peptisation of a metallic hydroxide can be obtained.

EXPERIMENTAL.

N/2 solutions of ferric and chromium chlorides were prepared by diluting stronger solutions which have been standardised gravimetrically. These two metals were specially chosen because of the ease with which their hydroxides can be obtained as positively and negatively charged colloidal solutions. The method of experimentation was almost the same as given in the previous paper. In order to save space only one typical result of adding alkali gradually to solutions of ferric chloride in presence of a constant quantity of glycerol is shown in Table I. The solutions were simultaneously tested with litmus paper, cataphoretic experiments being made by Burton's usual apparatus with distilled water at the top to investigate the nature of the charge on the particles, and the effect of coagulating ions was also studied in some cases. Chromium hydroxide has been considered to be completely

peptised when the solution became clear both in reflected and transmitted light within five minutes of mixing the solutions.

TABLE I.

Peptisation of Ferric Hydroxide.

Ferric chloride = 0·5 milliequivalent.
Glycerol = 1·0 milliequivalent.   Total Volume = 10 c.c.

Amount of NaOH added (milliequivalents.)	Results and Remarks.
0·333	Clear in transmitted and reflected light ; acid ; positively charged ; coagulated easily by K_2SO_4.
0·37	Slightly turbid ; clears after 5 minutes ; acid ; positive.
0·444	Turbid ; does not clear or settle; acid ; cataphoretic movement difficult to determine.
0·50	Gelatinous precipitate which settles down comparatively rapidly ; neutral.
0·555	Turbid ; does not settle easily ; alkaline ; cataphoretic movement difficult to determine.
0·629	At first turbid but becomes clear within a minute or two ; alkaline ; negatively charged ; coagulated readily by small concentrations of $BaCl_2$.
0·70	Clear both in transmitted and reflected light. Colloid negative.

From this table it will be observed that the range of instability of the peptised hydroxide lies between 0·4 to 0·6 milliequivalents of alkali, whilst with a lower or higher concentration of alkali, the colloid can be obtained either as positively charged or negatively charged particles. With chromium chloride solutions almost indentical results were obtained, the range of instability being practically the same. At the neutralisation point, namely with 0·5 milliequivalents of alkali, the chromium hydroxide separated readily

as a flocculent precipitate, but beyond this concentration range, the hydroxide could be easily obtained either as positively or negatively charged colloid. Since chromium hydroxide can be peptised by alkali alone (*Cf.* Herz and Fischer, *Zeit. anorg. Chem.*, 1902, **31**, 354 ; 1904, **40**, 39 ; Nagel, *J. Phys. Chem.*, 1915, **19**, 569) some observations are given in Table II, showing the effect of glycerol. The total volume was 15 c.c.

<div align="center">TABLE II.</div>

<div align="center">*Peptisation of Chromium Hydroxide.*</div>

Amount of chromium (milliequivalent) peptised.	Amount of NaOH necessary.	Amount of glycerol necessary for peptisation by 1·84 milliequivalents of alkali.
0·50	2·396	......
1·00	3·318	0·9
1·10	3·50	1·25
1·20	3·70	1·55

The effect glycerol will be made more clear by the following results : 0·5 milliequivalent of chromium requires approximately 1·65 milliequivalents of alkali for peptisation when the total volume is 10 c.c. If, however, one millimole of glycerol is added, 0·7 milliequivalent of alkali is sufficient. In presence of 1·5 millimoles of glycerol, 0·63 milliequivalent of alkali would be sufficient. With higher amounts of glycerol however no further reduction in the amount of alkali can be obtained, because the range of instability has nearly been reached. It should be stated here that the range of instability given above is only for the particular concentration of the metal peptised. If higher concentrations of the metals are used, then the range of instability also becomes greater. Thus with 1 milliequivalent of iron, the range of instability was approximately 0·8 to 1·2 milliequivalents of alkali.

In the previous paper attention has been drawn to the specific protecting powers of different non-electrolytes. Curiously enough, this specific property does not influence the amount of alkali necessary for peptisation when the non-electrolytes are present in

great excess. The specific action is only apparent when the minimum amount of non-electrolyte necessary for preventing, the formation of the precipitate is present. Thus the effects of cane sugar and glycerol may be compared with each other. Cane sugar is a better protective agent than glycerol in the case of ferric hydroxide. When the concentration of ferric chloride is 0·5 milliequivalent and total volume 10 c.c., then in presence of 0·7 millimoles of either sucrose or glycerol, the amount of alkali necessary for peptisation is 0·703 milliequivalent. When however 0·5 millimole of, sucrose or glycerol is present, the amounts of alkali necessary are respectively 0·74 and 0·962 milliequivalents. Thus with low concentrations of the non-electrolytes, their specific powers for protection becomes manifest. Similar results were also obtained with chromium hydroxide.

From the foregoing results it can be stated definitely that *the peptisation of metallic hydroxides, in general, cannot be obtained unless an excess of alkali is present in the solution.* In the particular cases of iron and chromium chlorides in presence of non-electrolytes, the reaction with caustic soda is thus of an exactly similar nature to that found by Lottermoser (*J. pr. Chem.*, 1905, **72**, 39 ; 1906, **73**, 374 ; *Zeit. physikal. Chem.*, 1907, **60**, 451) in the case of silver nitrate and potassium iodide, where an excess of either reagent would facilitate and was necessary for the formation of a colloid, but in exactly equivalent proportion, a precipitate would result,—a fact which can be explained on the views of Powis (*Zeit. physikal. Chem.*, 1915, **89**, 186) regarding the existence of a critical potential below which the colloid is unstable. Carrying this analogy further, we can say that the peptisation of the metallic hydroxides is an ionic one like that of the silver halides and is brought about by the preferential adsorption of the constituent ions of the colloid, namely OH' or the metal ion or may be in some cases H° ions, and thus the role played by the non-electrolyte must be considered to be a secondary one. It is however difficult to say at present how the non-electrolytes act, but a plausible hypothesis is that the adsorbed layer of the non-electrolyte inhibits the growth of the metallic hydroxide particles and keeps them more hydrated, and thus permits of their ready peptisation by the hydroxyl ions. This phenomenon would therefore be similar to those observed by Marc and others (Marc and Wenk, *Zeit. physikal. Chem.*, 1910, **68**, 112 ; also Freundlich, *Zeit. physikal. Chem.*, 1910, **75**, 245 ; "Kapillarchemie," Eng. Trans. p. 329, 1926 ; Pickardt, *Zeit. physikal.*

Chem., 1902, **42**, 17 ; Padoa and Galeati, *Gazz. chim. ital.*, 1904, **35**, I, 181) on the growth of nuclei in the formation of a new phase. Whatever may be the explanation, it is quite clear that *the non-electrolytes are not functioning as the peptising agents in the usual sense of the term, and we have to consider the hydroxyl ions as the real peptising agents in those cases where excess of hydroxyl ions are present.* This is in accord with the electro-kinetic behaviour shown by the peptised hydroxides.

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Pyrylium Salts and *Spiro*-Dipyrans.   Part II.   Condensation Products from Methylethyl ketone and o-Hydroxy Aldehydes.

By Satish Chandra De.

In Part I (this *Volume*, p. 23) it was shown that α-alkylated acetoacetic ester condenses with o-hydroxy aldehydes to form o-hydroxy styryl benzo-(or naphtho-)-pyrylium salts. In the present communication are recorded the results of the action of methylethyl ketone on o-hydroxyaldehydes. In these the reactions of methyl-ethylketone closely resemble those of the α-alkylated acetoacetic ester. The reaction proceeds in two stages as before (*loc. cit.*). In the first stage one molecule of the aldehyde condenses with one of the ketone to produce a pyrylium salt. In the second stage this salt condenses with another molecule of the aldehydes to yield an o-hydroxy styryl benzo-(or naphtho-) pyrylium salt. But the presence of two reactive groups in methylethyl ketone may admit of two possible reactions (a) and (b), as shown in the following formulae :

(IIa)

(IIIa)

(IIb)

(IIIb)
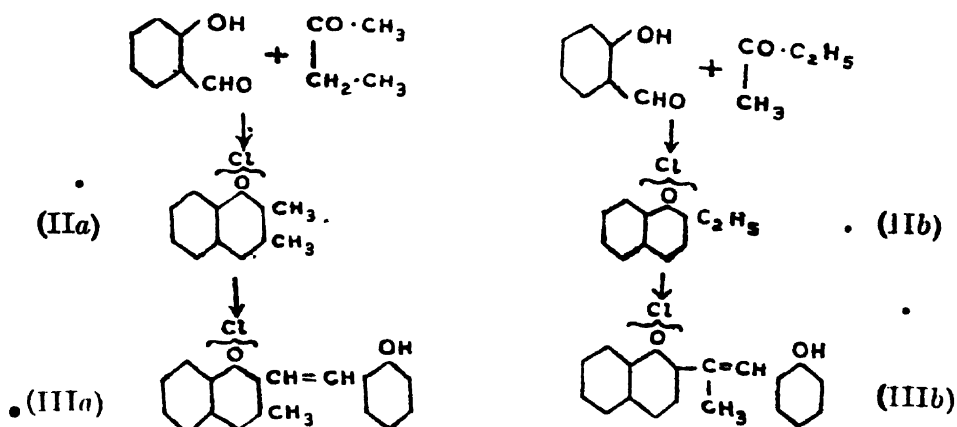
Under the condition (experimental part) the reaction takes the course (*a*) : the hydroxy styryl benzopyrylium chloride resulting from salicylaldehyde and methylethyl ketone is identical with the 3-methyl 2-(o-hydroxystyryl)-benzopyrylium   chloride   (III *a*)   derived   from

salicylaldehyde and 2:3-dimethylbenzo-pyrylium chloride (II *q*) ; also the pyrylium salt obtained from β-naphthol-α-aldehyde is the same whether methylethyl ketone or α-methyl acetoacetic ester is used.

The pyrylium salts are decomposed by alkali into colourless pseudo-bases which, on heating with hydrochloric acid, are converted into the pyrylium salts again. The *spiro*-dinaphthopyrone undergoes a colour change from white to blue-violet when heated with solvents, such as benzene, toluene and alcohol, which disappears again on cooling,—a property which is absent in the *spiro*-dibenzopyrans.

Attempts to prepare compounds having the formulae (II*b*, III*b*) are being made by a different method and will be described in a subsequent communication.

Experimental.

3-*Methyl-2-(o-hydroxystyryl)-benzopyrylium Chloride* (III*a*).

Into a mixture of salicylaldehyde (20 g.) and methylethylketone (6·0 g.) dissolved in ether (50 c.c.) hydrogen chloride gas was passed. The solution at once turned deep red and after a few minutes crystals began to separate. The hydrochloric acid gas was passed till the mixture was filled with a thick paste of crystals. This was filtered and washed with ether. Crystallised from acetic acid in dark needles having a metallic lustre, it has the melting point 198°. It was dried over caustic potash in vacuum and analysed. (Found : Cl, 11·62. $C_{18}H_{15}O_2Cl$ requires Cl, 11·89 per cent.).

The *ferric salt* can be obtained in red colour from the acetic acid solution of ferric chloride and the pyrylium chloride. The *perchlorate* can similarly be obtained by adding perchloric acid.

3-*Methyl*-spiro-*dibenzopyran*.
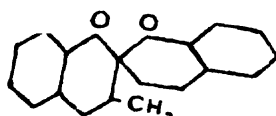
By adding ammonia to the aqueous solution of the pyrylium chloride, the pseudo-base was obtained as a white product, mixed

with tarry matter. It was purified by crystallisation from ligroin; m.p. 80°. (Found : C, 82·12 ; H, 5·56. $C_{18}H_{14}O_2$ requires C, 82·4 H, 5·34 per cent.).

3-Methyl-7-hydroxy-2-(2' : 4'-dihydroxystyryl)-benzo-pyrylium Chloride.
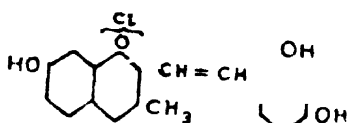
In a solution of resorcylaldehyde (8 g.) and methylethylketone (2 g.) ·d in ether (20 c.c.) hydrochloric acid gas was passed till the mixture was saturated with the gas. Within a short time the solution assumed a violet colour and was filled with highly coloured crystals. After several hours' standing the crystals were filtered and washed with ether. Crystallised from acetic acid it forms green-violet crystals with a metallic lustre, m.p. 290°. It was dried in vacuum over caustic potash and analysed. (Found : Cl, 10·34. $C_{18}H_{15}O_4Cl$ requires Cl, 10·74 per cent.).

From the acetic acid solution of the chloride, the *ferric salt* can be obtained by adding ferric chloride as violet-red needles.

3-Methyl-7 : 7'-dihydroxy-spiro-dibenzopyran.
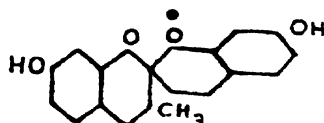
The colourless base was obtained by shaking the chloride with aqueous ammonia and was crystallised from alcohol. On heating with concentrated hydrochloric acid it was converted into the coloured chloride. (Found : C, 73·21 ; H. 4·92. $C_{18}H_{14}O_4$ requires C, 73·47 ; H, 4·76 per cent.).

3-Methyl-2-(o-hydroxy-a-benzostyryl)-β-naphtho-pyrylium Chloride.
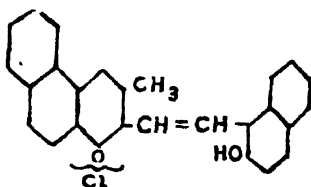
It was obtained from β-naphthol-a-aldehyde (11 g.) and methyl-ethylketone (2·4 g.) dissolved in acetic acid on saturating the solution with hydrochloric acid gas. After about 2 days the chloride separated in green crystals with a metallic lustre. This was filtered, washed with ether and crystallised from acetic acid and dried over caustic potash in vacuum. It did not melt at 290°. (Found: C, 77·97 ; H, 4·35. $C_{26}H_{19}O_2Cl$ requires C, 78·29 ; H, 4·76 per cent.).

The *ferric salt* can be obtained in greenish-red colour by adding ferric chloride to the acetic acid solution of the chloride.

3-Methyl-spiro-dinaphthopyran.
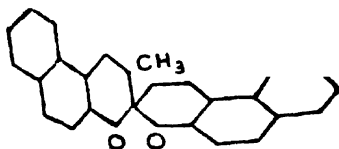
It was obtained by decomposing the chloride with ammonia. The impure product was purified from benzene when it formed colourless crystals, m.p. 201°. (Found: C, 86·28 ; H, 5·21. $C_{26}H_{18}O_2$ requires C, 86·15 ; H, 5·02 per cent.).

On heating with concentrated hydrochloric acid the pseudo-base is converted into the coloured chloride. On warming with benzene, toluene and alcohol it undergoes a colour change from white to blue-violet which disappears again on cooling.

My best thanks are due to Prof. J. C. Ghosh and Dr. P. C. Guha for their kind interest and encouragement during the course of the reaction.

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Interaction of Mercaptans with Phthalic Anhydride and Phthalyl Chloride.

By Gopal Chandra Chakravarti and Jogendra Mohan Saha.

The condensation of phenols with anhydrides of dibasic acids has been extensively studied, the reaction giving rise to important dyestuffs belonging to the triphenylmethane series. No attempt appears as yet to have been made to condense mercaptans with these anhydrides in order to obtain the thio-analogues of these dyestuffs. The present investigation was undertaken with a view to bring about this reaction. Difficulty was encountered in the choice of a suitable condensing agent. Sulphuric acid, dry hydrochloric acid gas, anhydrous zinc chloride containing hydrogen chloride, and zinc chloride alone were tried and had to be rejected. The condensation between phthalic anhydride and aromatic mercaptans was, however, effected by employing phosphorus pentoxide.

The products, when isolated, lacked all the characteristic properties of phthaleins, *e.g.*, they were colourless, crystalline substances, insoluble in alkalis. The phthalein condensation evidently did not take place. The mercaptanic hydrogen atoms, owing to their enhanced reactivity are eliminated (as water) in preference to the hydrogen atoms in the *ortho-* or *para*-position to the thiol group. In the reaction either the ketonic or the lactonic oxygen atom of the anhydride may be involved, giving rise to (I) or (II).

$$C_6H_4 < \begin{matrix} CO \\ \underset{\underset{RS \;\; SR}{\wedge}}{C} \end{matrix} >O \qquad\qquad C_6H_4 < \begin{matrix} COSR \\ COSR \end{matrix}$$

$$(I) \qquad\qquad\qquad (II)$$
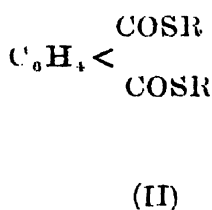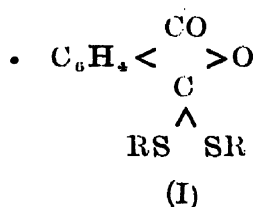
A choice between the thio-phthalide and the thioester constitution was arrived at from the fact that the compounds are not hydrolysed even by continued boiling with aqueous alkali. Had the products conformed to formula (I), the lactonic ring should have been opened by the treatment. Evidently thioesters of formula (II) are the exclusive products of the reaction. This view is supported by the fact

that various aliphatic mercaptans condense with phthalic anhydride in the same way.

The above results led the authors to investigate the action of the mercaptans on phthalyl chloride, which is known to exist in two tautomeric modifications,

$$C_6H_4 < \genfrac{}{}{0pt}{}{CO}{CCl_2} > O \quad \text{and} \quad C_6H_4 < \genfrac{}{}{0pt}{}{COCl}{COCl}$$
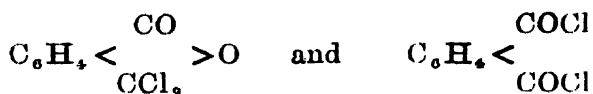
In fact reactions in support of both these structures have long been known. Phthalyl chloride has been prepared in two isomeric forms by Ott (*Annalen*, 1912, **392**, 245) and Csanyi (*Monatsh*, 1919, **40**, 81). In the present instance phthalyl chloride was prepared by heating the anhydride for several hours with an equimolecular quantity of phosphorus pentachloride at 200° (*Annalen*, 1887, **238**, 329). The chloride prepared in this way has been described by various investigators as reacting in either of the two tautomeric forms according to the conditions of the reaction. But the products of the condensation of the mercaptans with phthalyl chloride were found to be identical with those derived from the anhydride. With mercaptans at least phthalyl chloride behaves as if it had the symmetrical structure.

The constitution (I, R=Ph) assigned to the product of the réaction between phthalyl chloride and lead phenyl mercaptide by Troeger and Hornung (*J. pr. Chem.*, 1902, [ii], **66**, 345) seems to be erroneous. The substance, prepared by them, crystallises in glisten ing leaflets, m. p. 84-85°. The present authors obtained two compounds by the condensation of phthalyl chloride with phenyl mercaptan. One is identical with Troeger and Hornung's whilst the other crystallises in colourless granules, m. p. 101°. But none of these could be hydrolysed by boiling with aqueous alkalis which indicates that neither has the lactonic structure adopted for one of them by Troeger and Hornung. These two compounds are isomeric and the difference between them is not yet clear.

Bis-β-naphthyl thiophthalide prepared by Troeger and Hornung (*loc. cit.*) is described as a compound crystallising from alcohol and melting at 153-54°. The authors obtained a product from phthalyl chloride and β-naphthyl mercaptan which is sparingly soluble in alcohol and on crystallising from amyl alcohol melts at 70° and froths on further rise of the temperature. The latter compound had all the properties of a thiophthalate.

These thio-esters can possibly be utilised in the synthesis of the hitherto unknown monothiophthalic and dithiophthalic acids. The preliminary part of this investigation is complete and will form the subject matter of a later communication.

EXPERIMENTAL.

Phenyl Mercaptan and Phthalic Anhydride.

Two molecules of phenyl mercaptan (4·4 g.) and one molecule of phthalic anhydride (6 g.) were heated together at 130-140° and, to the liquid mixture phosphorus pentoxide (3 g.) was added and well stirred with a glass rod. After about three hours' heating the liquid was poured off leaving a black mass which was mostly phosphoric acid, tarry matter, and a small amount of the reaction products. The product which became semi-solid on cooling was dissolved in benzene, the solution was shaken with a dilute alkaline solution (2 to 3 times) and then well washed with water to remove alkali. It was then filtered, dehydrated with fused calcium chloride, again filtered and evaporated. The crystalline residue was dissolved in hot alcohol, boiled with animal charcoal, filtered and concentrated. The product, on recrystallisation, consisted of fine glistening leaflets of diphenyl dithiophthalate, m.p. 84-85°. (Found: S, 18·21.* $C_{20}H_{14}O_2S_2$ requires S, 18·28 per cent.)

The alcoholic mother-liquor was diluted with water until a turbidity was produced and then allowed to stand. A voluminous, granular, crystalline precipitate was obtained which was recrystallized from dilute alcohol, each time rejecting the first fraction of the crystals,; m.p. 101°. (Found: C, 69·1 ; S, 18·97. $C_{20}H_{14}O_2S_2$ requires C, 68·57 ; S, 18·28 per cent.).

Phthalyl Chloride and Phenyl Mercaptan.

Two molecules (5·5 g.) of phenyl mercaptan were heated under reflux with 1 molecule of phthalyl chloride (5 g.) in dry benzene solution for 6-7 hours. Copious evolution of hydrochloric acid gas took place. The solution, after cooling, was treated like the benzene

* In this and in all the subsequent estimations of sulphur, the Carius' method was supplemented by fusion of the sodium salt of the sulphonic acid with potassium nitrate and sodium carbonate.

solution in the previous experiment and two compounds, one melting at 84-85° and the other melting at 101°, identical respectively with the compounds previously prepared, were obtained.

p-Bromothiophenol and Phthalic Anhydride.

A mixture of two molecules (4 g.) of the mercaptan and one molecule (1·5 g.) of the anhydride was heated to 130-140° and phosphorus pentoxide (2 g.) was added to the liquid mass and well stirred. The heating was continued for three hours and the temperature was finally raised to 160-70°. While hot, the liquid mass was poured off leaving behind a tarry material as before. The liquid, which solidified on cooling, was shaken with a small quantity of cold alcohol. The residue was dissolved in hot alcohol, boiled with animal charcoal and filtered hot. White granular crystals of dibromodiphenyl dithiophthalate were obtained, m.p. 186-188°. (Found: C, 47·16; H, 3·3. $C_{20}H_{12}O_2S_2Br_2$ requires C, 47·20; H, 2·4 per cent.).

The alcoholic extract, made in the cold, was evaporated to dryness and the residue was found to be mainly phthalic acid.

p-Bromothiophenol and Phthalyl Chloride.

One molecule of phthalyl chloride (2 g.) was heated to 130-40° and two molecules of the mercaptan (3·8 g.) were gradually added and the mass well stirred. Copious evolution of hydrochloric acid gas took place. The mass was heated for an hour and a half after all the mercaptan had been added, the temperature being finally raised to 160-70°. On cooling the mass solidified; it was shaken with cold alcohol and then crystallized from boiling alcohol. White granular crystals, m.p. 186-88°, identical with the previous compound, were obtained.

p-Iodophenyl Mercaptan and Phthalic Anhydride.

Two molecules of the mercaptan (4·7 g.), one molecule of the anhydride (1·5 g.) and phosphorus pentoxide (2 g.) were heated together as in the case of p-bromothiophenol. The crude reaction product was first washed with cold alcohol and then dissolved in hot benzene and precipitated with petroleum ether. The white, granular, light crystals of diiododiphenyldithiophthalate were well washed with petroleum ether; m.p. 181-82°. (Found : C, 39·9; H, 2·6. $C_{20}H_{12}O_2S_2I_2$ requires C, 39·8; H, 2·0 per cent.).

p-*Iodothiophenol and Phthalyl Chloride.*

One molecule of the acid chloride (2 g.) and two molecules (4·7 g.) of the mercaptan were taken, and the experiment conducted as in the case of the p-bromothiophenol. The crude product was purified as in the previous case. White granular crystals, m.p. 181-82°, identical with the previous compound were obtained.

p-*Tolyl Mercaptan and Phthalic Anhydride.*

The mercaptan (5 g.), the anhydride (3 g.) and phosphorus pentoxide (3 g.) were employed, and the experiment was conducted in a manner similar to that with p-bromothiophenol. The product, ditolyl dithiophthalate, was crystallized from hot alcohol with previous boiling with animal charcoal. White, needle-like, light crystals, m.p. 149°. (Found : C, 69·76 ; H, 5·3. $C_{22}H_{18}O_2S_2$ requires C, 69·84 ; H, 4·8 per cent.).

p-*Tolyl Mercaptan and Phthalyl Chloride.*

The mercaptan (5 g.) and the acid chloride (4 g.) were employed and the experiment conducted as in previous cases. The crude product on purification and crystallization from alcohol, gave white, needle-like crystals, m.p. 149°, identical with the previous compound.

β-*Thionaphthol and Phthalic Anhydride.*

The mercaptan (4·8 g.), the anhydride (2·2 g.) and phosphorus pentoxide (2 g.) were taken and the experiment conducted as in previous cases. The cooled oily crude product was first washed with cold alcohol and then dissolved in hot acetone and precipitated with petroleum ether, the product solidified after a time. It was then recrystallized either from amyl alcohol or a large amount of alcohol. Di-β-naphthyl thiophthalate forms white, fine, granular crystals, m.p. 70° with frothing on further heating. It is very soluble in carbon disulphide, chloroform, acetone, benzene, toluene, xylene or glacial acetic acid. (Found : C, 74·25 ; H, 3·99. $C_{28}H_{18}O_2S_2$ requires C, 74·70 ; H, 4·00 per cent.).

β-Thionaphthol and Phthalyl Chloride.

The mercaptan (3·2 g.) and the acid chloride (2 g.) were taken. The experiment was conducted and the crude product purified as before. White granular crystals, m.p. 70°, identical with the product already obtained.

Benzyl Mercaptan and Phthalic Anhydride.

The mercaptan (5 g.), acid anhydride (3 g.) and phosphorus pentoxide (3 g.) were taken and the experiment conducted as in previous cases. The dark brown crude oily product was dissolved in benzene and the solution was treated as before. Evaporation of benzene gave a deep brown thick oil. This was extracted with a small amount of ether leaving a small amount of brown solid residue. The etheral solution was filtered and evaporated. This process was repeated 10-12 times until a transparent deep brown heavy oil (dibenzyl dithiophthalate) was obtained. (Found : S, 17·43. $C_{22}H_{18}O_2S_2$ requires S, 17·00 per cent.).

Benzyl Mercaptan and Phthalyl Chloride.

The mercaptan (2·5 g.) and the chloride (2 g.) were employed and the experiment conducted as usual. The compound was purified as above. The product was a deep brown oil, identical with the previous product.

Ethyl Mercaptan and Phthalyl Chloride.

The sodium salt of the mercaptan (3·3 g.) was suspended in dry benzene and the acid chloride (4 g.) was added to it ; the mixture was refluxed for about three hours. The solution was filtered to remove sodium chloride, shaken with a dilute alkaline solution repeatedly and then washed with water, filtered, dried and again filtered and evaporated. The mobile brown oil thus obtained was distilled in a vacuum but it decomposed. So it was purified by repeated extraction with small amount of ether as in the case of benzyl mercaptan compound. Diethyl dithiophthalate is soluble in alcohol, ether, acetone and benzene. (Found : S, 24·63. $C_{12}H_{14}O_2S_2$ requires S, 25·19 per cent.).

Propyl Mercaptan and Phthalyl Chloride.

The mercaptan (4·5 g.) and the acid chloride (6 g.) were heated in a sealed tube in the water-bath for about 6 hours. The crude

brown oil was next treated in the manner employed in the case of benzyl mercaptan. Vacuum distillation was also tried: the substance decomposed partly, a slightly brown mobile oil being obtained at 26 mm. pressure and 229-32°. The oil is soluble in alcohol, ether or benzene. (Found : S, 23·44. $C_{14}H_{18}O_2S_2$ requires S, 22·69 per cent.).

Butyl Mercaptan and Phthalyl Chloride.

The mercaptan (3·6 g.) and the acid chloride (4 g.) were heated together under reflux for about 3 hours. The deep brown oil was repeatedly shaken with dilute alkali. It was then extracted with ether and the solution well washed with water, filtered, dried, again filtered and evaporated : a light brown oil was obtained which was kept in vacuum for several days. Fine white needle-shaped crystals deposited which were separated. The oil, when crystals no longer separated, was dissolved in a small amount of ether. The solution was filtered and evaporated, and on analysis was found to be the disulphide of the mercaptan. The crystals were pressed on porous plate and then repeatedly crystallized from petroleum ether. White needle-shaped crystals (dibutyl dithiophthalate), m.p. 56-57°. (Found : S, 21·34. $C_{16}H_{22}O_2S_2$ requires S, 20·64 per cent).

Ethylene Mercaptan and Phthalyl Chloride.

The mercaptan (1·9 g.) and the acid chloride (4 g.) were heated together at 110-20° for an hour and a half. The cooled solid mass was washed with cold alcohol and crystallized from hot alcohol. White crystals of diethylenesulphide dithiophthalate, m.p. 169°, were obtained. (Found : C, 51·2 ; H, 3·97. $C_{12}H_{12}O_2S_4$ requires C, 50·7 ; H, 4·2 per cent.).

This experiment was repeated with twice the amount of mercaptan, when the same product was obtained in larger yield.

The authors take this opportunity of expressing their indebtedness to Sir P. C. Ray for the kind and helpful interest taken by him in this investigation.

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*β*z-tetrahydroquinazolines.

By Prafulla Chandra Mitter and Ashutosh Bhattacharya.

Although pyrimidine and quinazoline derivatives have been known for a long time and their properties thoroughly studied, very few of their reduction products are known. Pinner (" Die Imidoether," p. 292), in the course of his investigation on the reactivity of the *β*-ketonic esters with amidines, found that a tetrahydroquinazoline derivative is obtained by the action of amidine hydrochloride on succino-succinic ester according to the following scheme : —

(I).
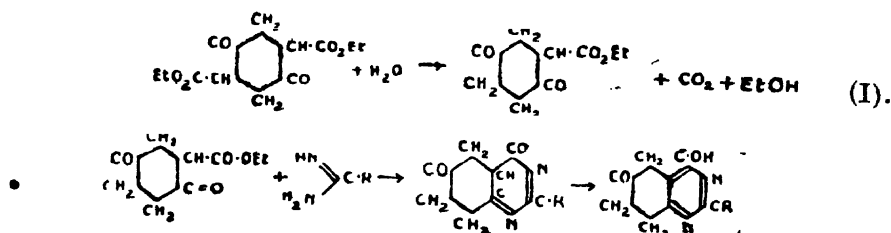
•Now as succino-succinic ester has two *β*-diketonic groupings in the skeleton, one molecule of succino-succinic ester may react with two molecules of amidine unless carbon dioxide splits off as in (I).
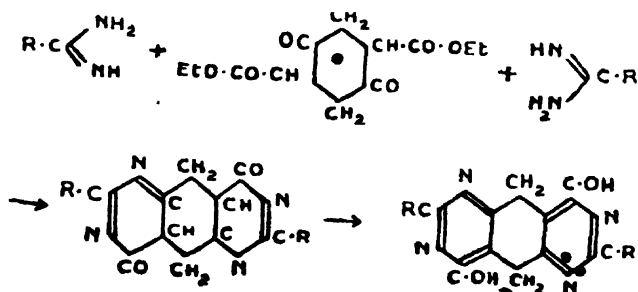
It was actually found by Pinner that when aliphatic amidines were used, the former reaction (*i.e.*, splitting off of CO_2 and the condensation with amidines afterwards) preponderated; but in the

case of aromatic amidines both the reactions took place and he had to experience considerable difficulty in isolating the pure product. It was also found by him that the product
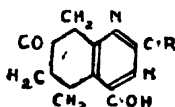
so formed in the case of aliphatic amidines is readily oxidized by the oxygen of the air in alkaline solution to a dihydroxy-quinozaline (II).
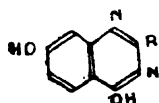
(II).

The compounds obtained by Pinner are the only known instances of quinazoline derivatives in which the benzene ring is reduced. Attempts have been made by different workers to reduce the quinazoline derivatives but in no case complete reduction was found to have taken place; only the pyrimidine ring was reduced leaving the benzene ring intact (*Ber.*, 1892, **25**, 3030). It is quite obvious, therefore, that in order to obtain *bz*-tetrahydroquinazolines, we have to start with β-diketones and β-ketonic esters with a reduced benzene ring and the substances most suitable for this purpose were found to be acetyl *cyclo*hexanone and ethyl *cyclo*hexan-1-one-6-carboxylate and their derivatives. *Bz*-tetrahydro-quinazolines are likely to give octahydroquinazolines on reduction but our attempts in this direction have so far not been attended with complete success. We have tried the action of benzamidine, *p*-toluamidine and guanidine on β-diketones and β-ketonic esters and attempt has also been made to prepare an octahydro-derivative by reducing a tetrahydro-derivative with sodium and alcohol.

The β-diketones and β-ketonic esters employed are the acetyl *cyclo*hexanone and its homologues and ethyl *cyclo*hexan-1-one-2-carboxylate and its homologues. Hydroxymethylene *cyclo*hexanone has also been used in one case.

In his pyrimidine synthesis, Pinner used potassium carbonate as the condensing agent; we also used the same reagent at first but the product obtained was of such an unstable nature that, on attempting to crystallise from alcohol, it decomposed into its

constituent components. Sodium ethoxide was then substituted for potassium carbonate solution. Tetrahydroquinazolines were obtained but the yield was poor—being only 33 per cent. of the acetyl *cyclo*hexanone used. To increase the yield, piperidine was subsequently used under similar conditions and the yield increased from 33 to 47 per cent. This use of piperidine as the condensing reagent was applied only in the case of β-diketones; but in the case of β-ketonic esters, sodium ethoxide was quite satisfactory, the yield being theoretical. It was also found that whereas in the case of β-diketones the whole thing required to be heated for 2 to 3 hours on the water-bath, in the case of β-ketonic esters the reation takes place even at the ordinary temperature though not completely,—confirming thereby the view that β-ketonic esters are, in general, more reactive than the β-diketones.

EXPERIMENTAL.

2-*Phenyl*-4-*methyl*-bz-*tetrahydroquinazoline*.

This was prepared by the condensation of benzamidine hydrochloride with acetyl *cyclo*hexanone in the presence of sodium ethoxide:
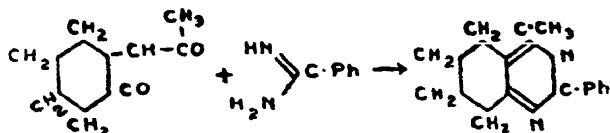
Benzamidine hydrochloride was prepared by Pinner's method from benzonitrile, and acetyl *cyclo*hexanone, according to the method of Borsche (*Annalen*, 1910, 377, 70) from *cyclo*hexanone.

Sodium (0·85 g.) was dissolved in a slight excess of absolute alcohol and benzamidine hydrochloride (3·35 g.) was added. Sodium chloride precipitated out and the benzamidine went into solution. Acetyl *cyclo*hexanone (3 g.) was then added and the mixture heated under a reflux on the water-bath for 2 hours. Excess of alcohol was driven off and the substance precipitated out by the addition of water. The yield of the crude product was 30 to 33 per cent. of the acetyl *cyclo*hexanone used. In later experiments by the use of piperidine as the condensing reagent, the yield increased from 33 to 47 per cent. of the acetyl *cyclo*hexanone used ; by the use of this reagent the mass becomes viscous and solidifies after 2

to 3 hours on the addition of water. It was crystallised from dilute alcohol ; white light feathery crystals, m· p. 103°, were obtained. (*Found: N, 12·88; C, 80·12; H, 7·44. C₁₅H₁₆N₂* requires N, 12·50; *C, 80·35; H, 7·14 per cent.*). Its *picrate* has the m.p. 144°-145°.

Condensation of Benzamidine Hydrochloride with Acetyl cyclo-Hexanone, with Potassium Carbonate as the Condensing Agent.

Benzamidine hydrochloride (1 g.) dissolved in 3 c.c. of water, was mixed with a saturated solution of potassium carbonate. The clear solution being mixed with acetyl *cyclo*hexanone (1·5 g.) immediately deposited an oily product which quickly solidified. The mixture was left overnight. The crude product melted between 106° and 109°. It was supposed that it might be an intermediate product; but in attempting to crystallise it either from alcohol or acetic acid it decomposed, setting the acetyl *cyclo*hexanone free.

2-p-Tolyl-4-methyl-bz-tetrahydroquinazoline.

p-Toluamidine hydrochloride, prepared according to the method of Pinner, was condensed with acetyl *cyclo*hexanone. The procedure is the same as in the case of benzamidine hydrochloride. From 3·64 g. *p*-toluamidine hydrochloride the yield of the crude product is 0·8 to 1 gm. It is crystallised from dilute alcohol : light feathery crystals, m.p. 129°-130°, are obtained. It is soluble in benzene, ether alcohol, acetone, ethyl acetate and petroleum ether. (Found : N, 12·39. C₁₆H₁₈N₂ requires N, 11·76 per cent.).

2-Amino-4-methyl-bz-tetrahydroquinazoline.

Finely powdered guanidine nitrate (2·7 g.) was condensed with acetyl *cyclo*hexanone (3 g.) in the presence of sodium ethoxide (0·37 g. Na). The procedure is the same as in the previous cases, the heating required in this case being 7 to 8 hours; yield of the crude product is 1·5 gm. It is crystallised from ethyl acetate; m.p. 177°-178°. (Found : N, 23·07. C₉H₁₃N₃ requires N, 25·76 per cent.).

2-Phenyl-4 : 8-dimethyl-bz-tetrahydroquinazoline.

2-Methyl-6-acetyl-1-*cyclo*hexanone (1·5 g.), prepared as in the case of acetyl *cyclo*hexanone from *o*-methyl-*cyclo*hexanone, was

condensed with benzamidine hydrochloride (1·58 g.) in the presence of sodium ethoxide (0·23 g. Na).

The procedure is the same as in the case of 2-phenyl-4-methyl-*bz*-tetrahydroquinazoline. Yield of the crude product is 0·7 gm. It is crystallised from dilute alcohol; m.p. 84°-85°. (Found: N, 11·48. $C_{16}H_{18}N_2$ requires N, 11·76 per cent.).

2-p-*Tolyl*-4 : 8-*dimethyl*-bz-*tetrahydroquinazoline.*

p-Toluamidine hydrochloride (1·6 g.) was condensed with 2-methyl-6-acetyl-1-*cyclo*hexanone (1·5 g.) in the presence of sodium ethoxide (0·23 g. Na). The procedure is the same as before. Yield of the crude product is 0·6 gm. It is crystallised from dilute alcohol; m.p. 95°. (Found: N, 11·74. $C_{17}H_{20}N_2$ requires N, 11·11 per cent.).

2-*Amino*-4 : 8-*dimethyl*-bz-*tetrahydroquinazoline.*

2-Methyl-6-acetyl-*cyclo*hexan-1-one (3 g.) was condensed with guanidine nitrate (2·2 g.) in the presence of sodium ethoxide (0·45 g. Na). The method of procedure is the same as in the case of 2-amino-4-methyl-*bz*-tetrahydroquinazoline. Yield of the crude product is 2 g. It is crystallised from alcohol; m.p. 103°-104°. (Found: N, 23·85. $C_{10}H_{15}N_3$ requires N, 23·72 per cent.).

2-*Phenyl*-4 : 7-*dimethyl*-bz-*tetrahydroquinazoline.*

3-Methyl-6-acetyl*cyclo*hexan-1-one (3 g.), prepared in the same way as acetyl *cyclo*hexanone from *m*-methyl*cyclo*hexanone, was condensed with benzamidine hydrochloride (3·5 g.) in the presence of sodium ethoxide (0·44 g. Na). The whole thing was heated on the water-bath, as in the previous cases, for 3 hours. In this case the smell of NH_3 was quite perceptible probably due to the decomposition of the amidine in the presence of sodium ethoxide. Yield of the crude product is 1 gm. It is crystallised from dilute alcohol; m.p. 111°-112°. (Found: N, 12·20. $C_{16}H_{18}N_2$ requires N, 11·76 per cent.).

2-p-*Tolyl*-4 : 7-*dimethyl*-bz-*tetrahydroquinazoline.*

3-Methyl-6-acetyl-*cyclo*hexan-1-one (3 g.) was condensed with *p*-toluamidine hydrochloride (3·3 g.) in the presence of sodium

ethoxide (0·44 g. Na). Procedure is the same as in the previous cases. Yield of the crude product is 0·5 gm. It is crystallised from dilute alcohol, m.p. 135°. (Found:N, 11·38. $C_{17}H_{20}N_{2}$ requires N, 11·11 per cent.).

B_z-TETRAHYDRO-HYDROXYQUINAZOLINES.

2-Phenyl-4-hydroxy-bz-tetrahydroquinazoline.

Ethyl *cyclo*hexan-1-one-2-carboxylate prepared according to the method of Kötz and Hesse (*Annalen*, 1905, **342**, 306) was condensed with benzamidine hydrochloride in the presence of sodium ethoxide. On adding the ester (2 g.) to the benzamidine hydrochloride (1·84 g.) in sodium ethoxide (0·26 g. Na) solution, a yellowish colouration developed with some evolution of heat, and the smell of NH_3 was quite perceptible. It was then heated on the water-bath for 2 hours. Yield of the crude product was 2·3 gm. It was crystallised from hot absolute alcohol mixed with animal charcoal. The crystals formed perfectly white, long needles, m.p. 238°. (Found:N, 12·04. $C_{14}H_{14}N_{2}O$ requires N, 12·39 per cent.).

2-p-Tolyl-4-hydroxy-bz-tetrahydroquinazoline.

Ethyl *cyclo*hexan-1-one-2-carboxylate (3 g.) was condensed with *p*-toluamidine hydrochloride (3 g.) in the presence of sodium ethoxide (0·4 g. Na).

The condensation was effected as in the previous case, the yield being 4 g. (almost quantitative). It was crystallised from hot alcohol mixed with animal charcoal in colourless needles, m.p. 255°—257°. (Found:N, 11·93. $C_{15}H_{16}N_{2}O$ requires N, 11·66 per cent.).

2-Amino-4-hydroxy-bz-tetrahydroquinazoline.

Ethyl *cyclo*hexan-1-one-2-carboxylate (3 g.) was condensed with guanidine nitrate (2·25 g.) in the presence of sodium ethoxide (0·4 g. Na). The experiment was effected as in the previous cases but though there was a rise of temperature there was no change of colour in this case. Yield of the crude product was 3·2 gm. It is insoluble in all the common solvents. For purification, this

substance was dissolved in acetic acid, filtered and the base reprecipitated by means of ammonium hydroxide. The precipitate was then thoroughly washed with water. It did not melt even above 300°. (Found: N, 25·42. $C_8H_{11}N_3O$ requires N, 25·45 per cent.).

2-*Phenyl*-4-*hydroxy*-8-*methyl*-bz-*tetrahydroquinazoline*.

Ethyl 2-methyl-*cyclo*hexan-1-one-6-carboxylate, prepared from *o*-methyl*cyclo*hexanone in the same way as ethyl *cyclo*hexan-1-one-2-carboxylate, was condensed with benzamidine hydrochloride in the presence of sodium ethoxide. On the addition of ethyl 2-methyl-*cyclo*hexan-1-one-6-carboxylate to the mixture of benzamidine hydrochloride and sodium ethoxide, a yellow colour developed. It was kept overnight and on experimenting with a part of it the next day, it was found that the reaction product did not go into solution although the reacting substances are all soluble in water. This shows that the reaction takes place even at the ordinary temperature though not completely. It was then heated on the water-bath for 2 hours. It is fairly soluble in hot alcohol, benzene and ethyl acetate. It crystallised from dilute alcohol, in tiny white needles, m.p. 200°. (Found: N, 12·0. $C_{15}H_{16}N_2O$ requires N, 11·66 per cent.).

2-p-*Tolyl*-4-*hydroxy*-8-*methyl*-bz-*tetrahydroquinazoline*.

The condensation was effected between ethyl 2-methyl-*cyclo*hexan-1-one-6-carboxylate (2 g.) with *p*-toluamidine hydrochloride (1·7 g.) using sodium ethoxide (0·25 g. Na) as the condensing reagent. The experimental details are the same as in the previous experiment. It was crystallised from absolute alcohol mixed with some animal charcoal. Needle-shaped crystals, m.p. 231°-133°, were obtained. (Found: N, 11·45. $C_{16}H_{18}N_2O$ requires N, 11·02 per cent.).

2-*Amino*-4-*hydroxy*-8-*methyl*-bz-*tetrahydroquinazoline*.

The condensation was effected as in the previous cases between ethyl 2-methyl*cyclo*hexan-1-one-6-carboxylate (2 g.) and guanidine nitrate (1·32 g.) in the presence of sodium ethoxide (0·25 g. Na). Yield of the crude product was 1·2 gm. It was crystallised from alcohol in very fine perfectly white needles, which do not melt even

at 300° (Found: N, 23·66. $C_9H_{13}ON_3$ requires N, 23·46 per cent.).

2-Phenyl-4-hydroxy-7-methyl-bz-tetrahydroquinazoline.

Ethyl 3-methyl-cyclohexan-1-one-6-carboxylate (2 g.) prepared from m-methylcyclohexanone according to the method of Kotz and Hesse (loc. cit.), was condensed with benzamidine hydrochloride (1·7 g.) in the presence of sodium ethoxide (0·25 g. Na) as in the previous experiments. Yield of the crude product was 1·8 gm. The condensation product was at first crystallised from dilute alcohol and then from benzene mixed with animal charcoal. Needles of bluish tinge, m.p. 214°−216, are obtained ; these are sparingly soluble in ligroin with which they were washed to get rid of the last traces of impurities. (Found: N, 12·23. $C_{16}H_{16}ON_2$ requires N, 11·66 per cent.).

2-p-Tolyl-4-hydroxy-7-methyl-bz-tetrahydroquinazoline.

The condensation was effected between ethyl 3-methylcyclo-hexan-1-one-6-carboxylate (2 g.) and p-toluamidine hydrochloride (1·7 g.) using sodium ethoxide (0·25 g. Na) as the condensing agent, as in the previous experiments. Yield of the crude product was 2·5 gm. The substance was crystallised from benzene ; m.p. 254°−256°. (Found: N, 11·09. $C_{16}H_{18}ON_2$ requires N, 11·02 per cent.).

2-Amino-4-hydroxy-7-methyl-bz-tetrahydroquinazoline.

The substance was prepared by condensing 3-methyl-cyclohexan-1-one-6-carboxylate (2 g.) with guanidine nitrate (1·32 g.) in the presence of sodium ethoxide (0·25 g. Na). Yield of the crude product was 2·2 g. It was crystallised from a large excess of hot water. The crystals are perfectly white needles, fibrous in nature. They do not melt above 300° but there is only a slight charring near about 310°. (Found: N, 23·83. $C_9H_{13}ON_3$ requires N, 23·46 per cent.).

2-Phenyl-bz-tetrahydroquinazoline.

Hydroxymethylene cyclohexanone prepared by the method of Wallach (Annalen, 1903, 329, 109) was condensed with benzamidine

hydrochloride using piperidine as the condensing reagent. Benzamidine hydrochloride (3·7 g.) was dissolved in alcohol, 1 c.c. of piperidine was added and subsequently the required quantity of hydroxymethylene *cyclo*hexanone (3 g.) introduced. It was then heated on the water-bath for six hours, when the solution became red. Excess of alcohol was driven off and the product was precipitated out by means of water. Yield of the crude product was 2·4 gm. As the substance has a low m.p., it was thrice slowly crystallised from absolute alcohol at ordinary temperature ; m.p. 52°−53°. (Found : N, 13·52. $C_{14}H_{14}N_2$ requires N, 13·33 per cent.).

The condensation between hydroxymethylene *cyclo*hexanone and *p*-toluamidine hydrochoride and guanidine nitrate will be described in a later paper.

Reduction of 2-Phenyl-4-methyl-bz-tetrahydroquinazoline.

The substance (2 g.) was reduced with absolute alcohol (170 c.c.) and sodium (18·4 g.) under reflux condenser. After all the sodium had dissolved in alcohol, excess of alcohol was driven off and water added to dissolve sodium ethoxide when an oil floated on the surface of the water. There was also much tarry matter produced. The oil was extracted with ether, dried over sodium sulphate, and distilled in *vacuo*. Copious white fumes came out and only 4 or 5 drops of a heavy yellow oil could be collected. It had a very bad smell like that of a fish oil. It did not solidify even when it was kept in a desiccator for 7 days. A *picrate* of the substance was then prepared. The picrate melts at 240° whereas the picrate obtained from 2-phenyl-4-methyl-*bz*-tetrahydroquinazoline melts at 144°−145°. The quantity of picrate being very small, the original substance could not be regenerated. This will be investigated in a subsequent paper.

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Synthesis of Coumaryl-4-acetic Acid.

By D. B. Limaye.

4-Methyl-coumarin being required in connection with another problem, attention was directed to its preparation. The substituted coumaryl-4-acetic acids, as a class, lose carbon dioxide when heated (Dey, *J. Chem. Soc.*, 1915, **107**, 1806 ; Dey and Row, *J. Indian Chem. Soc.*, 1925, **1**, 278). It was thought that the unsubstituted acid would give the desired 4-methyl-coumarin. Reference to the literature showed that the unsubstituted acid was not known to exist.

This led me to attempt the synthesis afresh, with the result that coumaryl-4-acetic acid can be prepared easily, the procedure is making use of the general method laid down by Dey and Row (*J. Indian Chem. Soc.*, 1924, **1**, 112) as follows :—A sulphuric acid solution of acetone-dicarboxylic acid is prepared by mixing ten parts of citric acid with thirty parts of concentrated sulphuric acid and warming on the water-bath till the evolution of carbon monoxide ceases. On cooling, four parts of phenol followed by ten parts of sulphuric acid are slowly added with shaking and the reaction mixture is allowed to stand at the ordinary temperature (25°) for twenty-four hours. It is then poured into cold water and thoroughly extracted with ether. The acid is removed from the ethereal extract by alkali and is precipitated by dilute sulphuric acid. The yield of the crude acid amounts to 15 parts for 100 parts of phenol. The acid is purified by recrystallisation from water till it melts at 170° with decomposition. (Found : C, 64·5 ; H, 4·0. $C_{11}H_8O_4$ requires C, 64·7 ; H, 3·9 per cent. Neutralisation equivalent, 203·4. A monobasic acid $C_{11}H_8O_4$ requires 204).

The acid when heated slightly over its melting temperature and kept at that point for some time, lost carbon dioxide and gave a liquid which solidified on cooling. This on recrystallising from water or alcohol, was identified with 4-methyl-coumarin both by direct comparison and through its bromo-derivative. These facts are quite in agreement with a coumaryl-4-acetic acid constitution for the new acid.

Action of different Ring-closing Agents upon 4-R-Thio-semicarbazide-dithiocarboxylates and 4-R-semicar-bazide-dithiocarboxylates: Formation of different . Types of Thiobiazoles and Oxybiazoles.

By Praphulla Chandra Guha and Sunil Chandra Guha.

Methyldithiocarbazinate was first prepared by Busch (*J. pr. Chem.*, 1916, **93**, 59), and in the same paper he described mono- and di-alkyl-dithiocarbazinates of the type $NH_2 \cdot NH \cdot CS \cdot SR$ and $NH_2 \cdot N:C(SR) \cdot SR'$ respectively. In the present paper a thorough and systematic study of methyldithiocarbazinate as regards its action upon different carbimides and thiocarbimides has been made and the resulting semicarbazide-dithiocarboxylates and thiosemicarbazide-dithiocarboxylates have been subjected to the action of different ring-closing agents, *e.g.*, hydrochloric acid, sodium hydroxide solution, acetic anhydride, etc.

Thiocarbimides and carbimides react with the active hydrazino part of the methyldithiocarbazinate to yield 4-R-thiosemicarbazide-1-methyldithiocarboxylates and 4-R-semicarbazide-1-methyldithiocarboxylates, thus :—

$$R \cdot NCS + NH_2 \cdot NH \cdot CSSMe \longrightarrow RNH \cdot CS \cdot NH \cdot NH \cdot CSSMe$$
$$R \cdot NCO + NH_2 \cdot NH \cdot CSSMe \longrightarrow RNH \cdot CO \cdot NH \cdot NH \cdot CSSMe$$
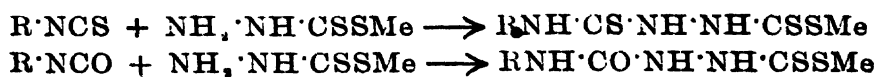
Phenyl-,tolyl-,xylyl-,allyl-*iso*thiocyanates and phenyl- and naphthyl-*iso*cyanates have thus yielded respectively the corresponding thiosemicarbazide-dithiocarboxylates (I, II, III, IV, see pp. 163, 166, 168 and 169) and semicarbazide-dithiocarboxylates (V, VI). .

The ring-closure of the above 4-R-thiosemicarbazide-1-methyldithiocarboxylates has been found to be really interesting. Phenylthiosemicarbazide-methyldithiocarboxylate loses one molecule of hydrogen sulphide when it is heated with alcohol with

31 .

the formation of 2-phenylimino-5-methylthiol-2:3-dihydro-1:8:4 thiodiazole, thus:

$$\text{PhNH·CS·NH·NH·CSSMe} \longrightarrow \underset{\substack{| \\ \text{SH}}}{\text{PhN:C}} \overset{\text{NH——N}}{\underset{\substack{\| \\ \text{SH}}}{}} \underset{\text{SH}}{\text{C·SMe}}$$

$$\xrightarrow[\longrightarrow]{-\text{H}_2\text{S}} \quad \underset{\substack{| \\ }}{\text{PhN:C}} \overset{\text{NH·N}}{\underset{\substack{\text{V} \\ \text{S}}}{}} \text{C·SMe} \qquad \qquad \ldots \text{ (VII).}$$
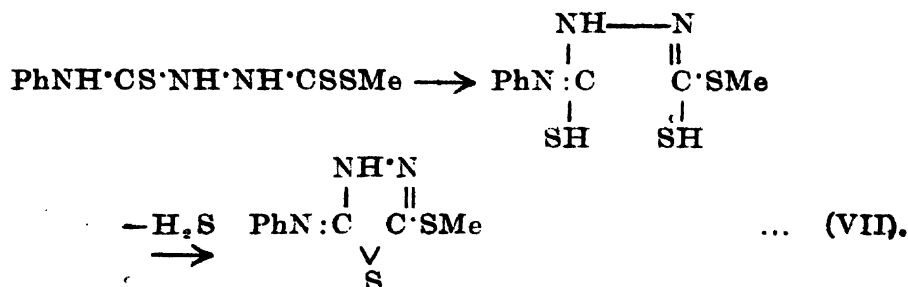
The same compound (VII) is also obtained when an aqueous solution of methyldithiocarbazinate hydrochloride is boiled with phenyl mustard oil. Presumably, 4-phenylthiosemicarbazide-1-methyl-dithiocarboxylate is formed and loses a molecule of sulphuretted hydrogen.

By the action of acetic anhydride, the acetyl derivative of compound (VII) is formed, and this can be hydrolysed so as to yield compound (VII).

By the action of hydrochloric acid upon phenylthiosemicarbazide-dithiocarboxylate, a molecule of aniline is split off and there is formed 2-thio-5-methylthiol-2:3-dihydro-1:3:4-thiodiazole, thus:

$$\underset{\substack{| \\ \text{NHPh}}}{\overset{\text{NH——N}}{\underset{\substack{\| \\ }}{\text{SC}}}} \underset{\text{SH}}{\overset{}{\text{C·SMe}}} \longrightarrow \underset{\substack{\text{V} \\ \text{S}}}{\overset{\text{HN—N}}{\text{SC}}} \text{C·SMe} + \text{PhNH}_2 \qquad \text{(IX)}$$
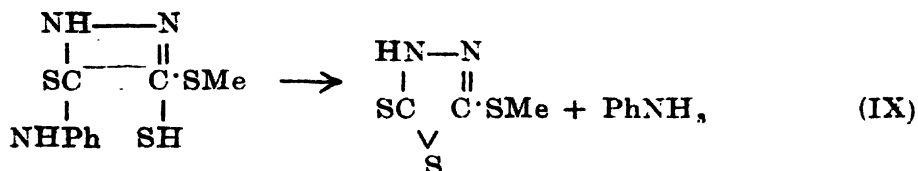
Ring-closure of phenylthiosemicarbazide-dithiocarboxylate has also been effected with sodium hydroxide solution. In this case however, the ring-closure is attended with the elimination of a molecule of methyl mercaptan. Thus there is formed 2-phenylimino-5-thiol-2:3-dihydro-1:3:4-thiodiazole :—

$$\underset{\substack{| \\ \text{SH}}}{\text{PhN:C}} \overset{\text{NH——N}}{\underset{\substack{\| \\ \text{SMe}}}{}} \text{C·SH} \xrightarrow{\text{NaOH}} \underset{\substack{\text{V} \\ \text{S}}}{\text{PhN:C}} \overset{\text{HN—N}}{} \text{C·SH} + \text{MeSH} \qquad \ldots \text{ (X)}$$
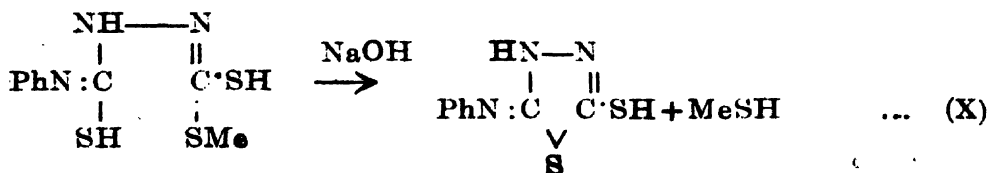
This compound was prepared by Freund and Imgart (*Ber.*, 1895, **28**, 956) from PhNH·CS·NH·NH·CS·NHPh by boiling with

concentrated hydrochloric acid and they wrongly called it phenyl-dithiourazole. Guha prepared a large number of such R-imino-thiol-thiobiazoles from $RNH \cdot CS \cdot NH \cdot NH_2$ and carbon bisulphide in presence of potassium hydroxide (*J. Amer. Chem. Soc.*, 1922, **44**, 1510).

The action of tolyl mustard oil upon methyldithiocarbazinate is peculiar and takes two different courses depending upon whether the solvent is taken in large or small quantity.

With a small quantity of alcohol, there is formed 4-tolyl-thio-semicarbazide-1-methyldithiocarboxylate, and with a larger quantity, there is formed 2-tolylimino-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thio-diazole (X).

Xylyl (and allyl) mustard oil reacts with methyldithiocarbazin-ate to give a mixture of 4 R-thiosemicarbazide-1-methyldithiocar-boxylate and 2-R-imino-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodia-zole of which the former is soluble in alkali whilst the latter is not.

The actions of acetic anhydride, hydrochloric acid, sodium hydroxide upon the tolyl, xylyl, and allyl compounds (II, III, IV) are exactly similar to those as observed with the corresponding phenyl compound (I) and thus compounds (XI—XVII) are formed.

Acetic anhydride reacts with phenyl and naphthyl semicarbazide-dithiocarboxylates (V and VI) to yield 2-R-imino-3-acetyl-5-methyl-thiol-2 : 3-dihydro-1 : 3 : 4-oxdiazoles (XVIII, XIX), thus :

$$RNH \cdot CO \cdot NH \cdot NH \cdot CSSMe \longrightarrow \begin{array}{c} AcN-N \\ | \quad \| \\ RN:C \quad C \cdot SMe + H_2S \\ \diagdown \diagup \\ O \end{array}$$
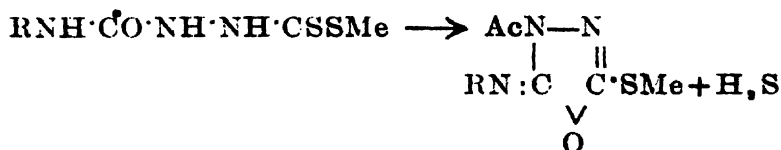
4-Phenyl-thiosemicarbazide-1-methyldithiocarboxylate. $PhNH \cdot CS \cdot NH \cdot NH \cdot CS_2Me$ (I).

Methyldithiocarbazinate (6 g.) was dissolved in warm absolute alcohol and phenyl mustard oil (7 g.) was gradually added and the mixture was continually shaken. The solution was allowed to stand overnight when a white precipitate was found to have formed which was filtered and crystallised from alcohol. The yield before crystal-lisation was quantitative but after crystallisation the yield was 10 gms., the loss being due to the formation of a ring compound, which remained in the mother-liquor. It melts at 143°-144° with

decomposition. Busch (*J. pr. Chem.*, 1916, **93**, 360) gives m. p. 136°-137°. (Found: N, 16·14. $C_9H_{11}N_3S_3$ requires N, 16·34 per cent.).

2 - *Phenylimino -5-methylthiol-2 : 3 - dihydro - 1 : 3 : 4 - thiodiazole* (VII).—The alcoholic mother-liquor from the above experiment was concentrated to half its bulk and treated with an equal volume of water. The white precipitate was crystallised from dilute alcohol; m.p. 132°-133°. It is extremely soluble in alcohol but insoluble in alkali. (Found: N, 18·41. $C_9H_9N_3S_2$ requires N, 18·83 per cent.)

The Acetyl derivative.—The above substance (1 g.) was heated with an excess of acetic anhydride under reflux for about 20 minutes and then poured into water when an oily mass was obtained which solidified on standing. It was crystallised from water; m.p. 153°-154°. (Found: N, 15·60. $C_{11}H_{11}ON_3S_2$ requires N, 15·85 per cent.)

Methyldithiocarbazinate Hydrochloride and Phenyl Mustard Oil: Formation of (VII).

Methyl-dithiocarbazinate (2·48 g.) was dissolved in an excess of dilute hydrochloric acid and phenyl mustard oil (2·8 g.) gradually added. The mixture was heated under reflux for 3-4 hours; on cooling a white solid mass was obtained. It was crystallised from dilute alcohol; m. p. 132°-133°. It is insoluble in dilute caustic soda solution and identical with compound (VII). (Found: N, 18·54. $C_9H_9N_3S_2$ requires N, 18·83 per cent.). Busch and Schmidt (*Ber.*, 1913, **46**, 2247) and Busch and Bichler (*J. pr. Chem.*, 1916, **93**, 360) give m. p. 126-127°.

Phenyl-thiosemicarbazide-dithiocarboxylate and Acetic Anhydride : Formation of 2-Phenylimino-3-acetyl-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiobiazole.

Phenyl-thiosemicarbazide-methyldithiocarboxylate (2 g.) was heated on a sand-bath with an excess of acetic anhydride under reflux for 15-20 minutes. The clear solution was poured into water when an oily mass was obtained which on standing solidified and was crystallised from water. Yield 1 gm. It is insoluble in dilute caustic soda solution: m. p. 153°-154°. (Found: N, 15·63.

$C_{11}H_{11}ON_3S_2$ requires N, 15·85 per cent.). It is identical with the acetyl derivative of compound (VII) ; mixed m. p. 153-154°.

Deacetylation of the above Compound.

The above compound (1 g.) was heated with concentrated hydrochloric acid (d 1·19) for 20 minutes. On cooling a white solid came down which was crystallised from dilute alcohol. It was identical with compound (VII); m. p. 132°-133°. (Found : N, 18·62. $C_9H_9N_3S_2$ requires N, 18·83 per cent.)

Treatment of Phenyl-thiosemicarbazide-methyldithiocarboxylate with Hydrochloric Acid : Formation of 2-Thion-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiobiazole (IX).

Phenyl-thiosemicarbazide-methyldithiocarboxylate (2 g.) was heated with an excess of concentrated hydrochloric acid (d 1·19) for 15 minutes. The reaction mixture, on cooling, yielded a white precipitate which was crystallised from water in needles; m. p. 143°-144°. Yield 1 gm. It is soluble in cold dilute sodium hydroxide solution. (Found : N, 17·29. $C_3H_4N_2S_3$ requires N, 17·07 per cent.).

2 : 5-Dimethylthiol-1 : 3 : 4-thiobiazole.

The above substance (0·8 g.) was dissolved in the calculated quantity of sodium hydroxide solution (1 mol. to 1 mol.) and was heated with methyl iodide (0·7 g.) and a few c.c. of methyl alcohol under reflux at 50°-60° for about 15 minutes. After removing the excess of methyl iodide, the solution was poured into water when an oil separated which did not solidify even on standing for several hours. It was then extracted with ether dried over fused calcium chloride, the ether removed and then kept in a vacuum desiccator, where it solidified after a few days and was crystallised from dilute alcohol. It is insoluble in alkali; m. p. 136° ; yield 0·1 gm. (Found : N, 15·52. $C_4H_6N_2S_3$ requires N, 15·73 per cent.).

Busch and Ziegele (*J. pr. Chem.*, 1899, **60**, 42) prepared the dimethyl compound by an entirely different method and gave the m. p. 136°. It might be mentioned here that the present method is the only method by which the mono-alkyl-derivatives of the thiobiazoledithiol can be obtained.

Treatment of Phenyl-thiosemicarbazide-methyldithiocarboxylate with Caustic Soda: Formation of 2-Phenylimino-5-thiol-2:3-dihydro-1:3:4-thiodiazole (X).

Phenyl-thiosemicarbazide-methyl-dithiocarboxylate (2 g.) was heated with 2N-sodium hydroxide solution under reflux. The reaction commenced within a few minutes as was indicated by the evolution of mercaptan. After six hours' heating the evolution of mercaptan ceased and the solution was after cooling acidified with dilute hydrochloric acid. The white precipitate thus obtained was crystallised from alcohol m. p. 215°-216°. (Found: N, 20·31. $C_8H_7N_3S_2$ requires N, 20·10 per cent.).

The Benzyl derivative.—The above substance (0·2 g.) was dissolved in alcoholic sodium hydroxide solution and was heated with benzyl chloride (0·22 g.) under reflux for 10-15 minutes. A white solid separated out which was washed with water and crystallised from dilute alcohol, m. p. 140°-141°. (Found: N, 14·21. $C_{15}H_{13}N_3S_2$ requires N, 14·05 per cent.).

The Methyl derivative.—The substance (1 g.) was dissolved in methyl alcoholic solution of sodium hydroxide and heated with methyl iodide (0·5 g.) under reflux at 50°-60° during 20-25 minutes. On pouring into water and standing for some time, a white solid separated which was washed with water and crystallised from alcohol ; m. p. 132°-133°. (Found: N, 18·63. $C_9H_9N_3S_2$ requires N, 18·83 per cent.). It is identical with compound (VII).

Methyldithiocarbazinate and p-Tolyl Mustard Oil (in a small quantity of alcohol): Formation of 4-p-Tolyl-thiosemicarbazide-1-methyldithiocarboxylate, p-TolNH·CS·NH·NH·CS$_2$Me.

Methyldithiocarbazinate (6·1 g.) was dissolved in the minimum quantity of alcohol and tolyl mustard oil (7·5 g.) was gradually added with shaking and the mixture allowed to stand overnight. The separated solid was crystallised in plates from benzene, m. p. 135°-136° (with decomp.). It is soluble in cold dilute sodium hydroxide solution. The yield is quantitative. (Found: N, 15·78. $C_{10}H_{13}N_3S_3$ requires N, 15·50 per cent.).

Methyldithiocarbazinate and p-Tolyl Mustard Oil (in a large quantity of alcohol): Formation of 2-Tolylimino-5-methylthiol-2:3-dihydro-1:3:4-thiodiazole (XI).

Methyldithiocarbazinate (3 g.) was dissolved in a large quantity of absolute alcohol and tolyl mustard oil (3:8 g.) gradually

added to it and the mixture kept overnight. No precipitate was found to have separated next day ; but after 4 or 5 days, a crystalline precipitate began to separate slowly with the evolution of sulphuretted hydrogen. After a week, the solid product was separated by filtration and crystallised in rectangular plates from dilute alcohol, m. p. 137°-138°. It is insoluble in dilute caustic soda solution. (Found: N, 17·38. $C_{10}H_{11}N_3S_2$ requires N, 17·72 per cent.).

Formation of the above compound can be enhanced by concentrating the alcoholic reaction mixture on a water-bath.

The *acetyl derivative* was prepared in the usual manner and was crystallised from water. It melts at 94°-95°, and the mixed melting point with the compound obtained from *p*-tolyl-thiosemicarbazide-dithiocarboxylate and acetic anhydride was also 94-95°. (Found: N, 15·42. $C_{12}H_{13}ON_3S_2$ requires N, 15·05 per cent.).

Deacetylation of the above Compound.

The acetyl compound was de-acetylated by heating with concentrated hydrochloric acid and the resulting compound was found, by analysis and mixed melting point, to be identical with the compound as obtained by the action of methyl iodide upon compound (XIII). (Found: N, 17·34. $C_{10}H_{11}N_3S_2$ requires N, 17·72 per cent.).

Tolyl-thiosemicarbazide-methyldithiocarboxylate and Acetic Anhydride : Formation of 2-Tolylimino-5-methylthiol-3-acetyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole (XII).

Proceeding in the same way as with the phenyl compound, 1·5 gm. of the thiodiazole derivative was obtained from 2 gm. of the dithiocarboxylate. It melted at 94°-95°. It was proved to be identical with the compound as obtained by acetylating compound (XI). (Found: N, 15·42. $C_{12}H_{13}ON_3S_2$ requires N, 15·05 per cent.).

Treatment of Tolyl-thiosemicarbazide-methyldithiocarboxylate with Hydrochloric Acid : Formation of 2-Thion-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole (IX).

The method of procedure was the same as with the phenyl compound. It melted at 143°-144°. It was proved to be identical

with compound (IX) obtained from phenyl-thiosemicarbazide-dithiocarboxylate. Presence of toluidine in the acid filtrate was proved.

Treatment of Tolyl-thiosemicarbazide-methyldithiocarboxylate by Sodium Hydroxide: Formation of 2-Tolylimino-5-thiol-2:3-dihydro-1:3:4-thiodiazole (XIII).

The method of preparation and isolation was the same as in the case of the corresponding phenyl compound (X). It was crystallised from alcohol, m.p. 215°-216°. (Found: N, 18·77. $C_9H_9N_3S_2$ requires N, 18·83 per cent.).

The Disulphide.—The above thiobiazole compound was dissolved in dilute caustic soda solution and an iodine solution (in potassium iodide) gradually added to it until no more was taken up. The yellow product so obtained could neither be crystallised nor purified from the common organic solvents, it being insoluble in all of them. It was repeatedly washed with dilute sodium hydroxide solution and water and then dried in a steam oven. It shrinks at 185° and melts at 210°-212°. (Found: N, 18·68. $C_{18}H_{16}N_6S_4$ requires N, 18·92 per cent.).

Methyldithiocarbazinate and Xylyl Mustard Oil: Formation of 4-Xylyl-thiosemicarbazide-1-methyl-dithiocarboxylate (III) *and* 2-*Xylylimino-5-methylthiol-2:3-dihydro-1:3:4-thiodiazole* (XIV).

Xylyl mustard oil (6·5 g.) was gradually added to an alcoholic solution of methyl-dithiocarbazinate (5 g.) under shaking and then allowed to stand for four days without the formation of any precipitate. The solution, on being concentrated on a water-bath, yielded a pasty mass which was treated with cold dilute sodium hydroxide solution in which it was found to be partially soluble. The alkaline filtrate on acidification with dilute hydrochloric acid gave a semi-solid mass which soon solidified. The solid could not be isolated in a pure state. So, further investigation was performed with this crude product (yield 2 g.).

2-Xylylimino-5-methylthiol-2:3-dihydro-1:3:4-thiobiazole.

The insoluble portion was thoroughly triturated with dilute caustic soda solution to remove any trace of the alkali-soluble compound, filtered, washed repeatedly with water and finally

crystallised from dilute alcohol, m. p. 135°-136°; yield 7 gms. (Found; N, 17.19. $C_{11}H_{13}N_3S_2$ requires N, 16·73 per cent.).

The *acetyl derivative* was prepared by heating the above compound with an excess of acetic anhydride under reflux for 15 minutes. It was crystallised from water; m.p. 128°-129°. It was proved to be identical with the compound obtained by the action of acetic anhydride upon xylyl-NH·CS·NH·NH·CSSMe. (Found : N, 14·46. $C_{13}H_{15}ON_3S_2$ requires N, 14·33 per cent.).

Action of Acetic Anhydride upon Xylyl-thiosemicarbazide-dithiocarboxylate : Formation of 2-Xylylimino-3-acetyl-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole (XV).

The crude dithiocarboxylate was heated with an excess of acetic anhydride under reflux for 15 minutes. It was then poured into water when an oily mass was obtained which soon solidified and was crystallised from water, m.p. 128°-129°. (Found : N, 14·67. $C_{13}H_{15}O N_3S_2$ requires N, 14·33 per cent.).

De-acetylation of the foregoing acetyl compound was effected by heating it with concentrated hydrochloric acid. It was identical with the alkali-insoluble compound obtained by the action of xylyl mustard oil upon methyldithiocarbazinate; m.p. 135°-136°. (Found : N, 17·20. $C_{11}H_{13}N_3S_2$ requires N, 16·73 per cent.).

Treatment of Xylyl-thiosemicarbazide-dithiocarboxylate with Hydrochloric Acid : Formation of 2-Thion-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole (IX).

The crude substance was heated with an excess of concentrated hydrochloric acid. The solid obtained on cooling was crystallised in needles from water, m.p. 143°-144°. It is soluble in dilute sodium hydroxide solution and is identical with the compound as obtained from phenyl- and tolyl-thiosemicarbazide-methyldithiocarboxylates on similar treatment.

Methyl-dithiocarbazinate and Allyl Mustard Oil : Formation of Allyl-thiosemicarbazide-methyldithiocarboxylate (IV) *and 2-Allylimino-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole* (XVI).

Allyl musard oil (5 g.) was gradually added to methyl dithiocarbazinate (6 g.) dissolved in absolute alcohol and the mixture well shaken and allowed to stand at ordinary temperature for four days.

As no precipitate came out, the solution was almost evaporated to dryness on the water-bath when a semi-solid product was obtained. It was then treated with cold dilute caustic soda solution and filtered. The filtrate on acidification with dilute hydrochloric acid gave a white precipitate which was purified by crystallisation from water; m.p. 139°-140°; yield 4 gms. (Found: N, 19·39. $C_6H_{11}N_3S_3$ requires N, 19·00 per cent.).

2-Allylimino-5-methylthiol-2:3-dihydro-1:3:4-thiodiazole (XVI).

The portion insoluble in alkali was washed repeatedly with water and was obtained in long rectangular crystals from boiling water. It shrinks at 75° and melts at 77°-78°. Yield 5 gms. (Found: N, 21·97. $C_6H_9N_3S_2$ requires N, 22·46 per cent.).

The *acetyl derivative* was prepared in the usual manner and crystallised from a small quantity of water. It shrinks at 85° and melts at 93°-94°. It is identical with the compound as obtained by the action of acetic anhydride upon the parent dithiocarboxylate (IV).

Allyl-thiosemicarbazide-dithiocarboxylate and Acetic Anhydride: Formation of 2-Allylimino-3-acetyl-5-methylthiol-2:3-dihydro-1:3:4-thiodiazole (XVII).

The dithiocarboxylate was heated with acetic anhydride under reflux for 15 minutes and was then poured into water and after some time a solid mass came out which was crystallised from a small quantity of water. It is insoluble in cold dilute caustic soda solution, shrinks at 85° and melts at 93°-94°. (Found: N, 18·63. $C_8H_{11}ON_3S_2$ requires N, 18·34 per cent.).

The *de-acetylation* of compound (XVII) was effected in the usual manner by heating with concentrated hydrochloric acid and the product was crystallised from water in long rectangular plates, m.p. 77°-78°. It was identical with compound (XVI). (Found: N, 22·14. $C_6H_9N_3S_2$ requires N, 22·46 per cent.).

Action of Hydrochloric Acid upon Allylthiosemicarbazide-dithiocarboxylate: Formation of 2-Thion-5-methylthiol-2:3-dihydro-1:3:4-thiodiazole (IX).

On heating the dithiocarboxylate with concentrated hydrochloric acid a crystalline mass was obtained which was crystallised in needles

from water, m.p. 143°-144°.   It is identical with the compound (IX) as obtained similarly from phenyl-, tolyl-, and xylyl-thiosemicarbazido-dithiocarboxylates.

Phenyl isocyanate and Methyl-dithiocarbazinate: Formation of 4-Phenylsemicarbazide-1-methyldithiocarboxylate (V).

From 2 gms. of methyl-dithiocarbazinate and 2 gms. of phenyl-isocyanate, 3·8 gm. of the product were obtained. The compound was crystallised from rectified spirit and was soluble in cold dilute alkali. It melts at 197°-198° with decomposition. (Found: N, 17·81. $C_9H_{11}ON_3S_2$ requires N, 17·42 per cent.).   Busch (*J. pr. Chem.*, 1916, **93**, 351) gives m.p. 190°.

Action of Acetic Anhydride upon the above Compound: Formation of 2-Phenylimino-3-acetyl-5-methylthiol-2:3-dihydro-1:3:4-oxybiazole (XVIII).

The above compound was heated with an excess of acetic anhydride under reflux for 15-20 minutes.   It was then poured in water when an oily mass separated out which solidified on standing for some time.   The product so obtained was crystallised from water; m.p. 139°-140°.   (Found: N, 16·42. $C_{11}H_{11}O_2N_3S$ requires N, 16·87 per cent.).

Naphthyl isocyanate and Methyl-dithiocarbazinate: Formation of 4-Naphthyl-semicarbazide-1-methyldithiocarboxylate (VI).

Naphthyl-isocyanate (2·4 g.) was gradually added to an alcoholic solution of methyl-dithiocarbazinate (3·3 g.) under vigorous shaking and the mixure was allowed to stand for some time when an insoluble white solid product was obtained. It was crystallised repeatedly from alcohol, m.p. 202°-203° (with decomposition). Yield quantitative.   It was soluble in dilute caustic soda solution. (Found: N, 14·21. $C_{13}H_{11}ON_3S_2$ requires N, 14·43 per cent.).

Ring-closure of the above Compound with Acetic Anhydride: Formation of 2-Naphthylimino-3-acetyl-5-methylthiol-2:3-dihydro-1:3:4-oxydiazole (XIX).

1·5 gm. of a white solid product were obtained by treating 2 gm. of the above compound with acetic anhydride.   It was crystallised

from dilute alcohol, m. p. 149°-150°. It was insoluble in alkali. (Found: N, 14·46. $C_{15}H_{13}O_2N_3S$ requires N, 14·05 per cent.).

Our thanks are due to Sir P. C. Râ y and Prof. J. C. Ghosh for the kind interest they have taken in this work.

Adsorption of Ions and of Sols at Interfaces and its Applications to certain Problems of Colloid Chemistry.

By N. R. Dhar.

Experiments on the adsorption of various electrolytes by sols as well as by freshly precipitated substances have been carried on in these laboratories for more than ten years. As adsorbents we have used hydrated manganese dioxide, ferric hydroxide, aluminium hydroxide, chromium hydroxide, stannic hydroxide, vanadium pentoxide, silicic acid, arsenious sulphide, antimony sulphide, barium sulphate, etc. In this communication I shall briefly state the important results obtained by us.[1]

We have observed that hydrated manganese dioxide mainly adsorbs the basic portions of salts making the neutral solutions acid after adsorption. Similarly barium sulphate in the course of its formation mainly adsorbs the acid radicles from neutral salts making the solutions distinctly alkaline.

From the experimental results on adsorption, which are available at present, we have come to the following conclusions : —

(1) The generally accepted view that an ion, which is highly adsorbed also possesses a high coagulating power is not supported by experiments on adsorption.

(2) There is no justification for the assumption that the greater the valency and hence the coagulating power of an ion, the greater is its adsorption.

(3) On the other hand, experiments on the coagulation and adsorption of different ions by sols of HgS, Sb_2S_3, $Al(OH)_3$, $Fe(OH)_3$, V_2O_5, MnO_4 etc., strongly support our view that the greater the valency of an ion, the less is the amount of adsorption.

[1] *Zeit. anorg. Chem.*, 1922, **121**, 135 ; 1926, **152**, 399, 405 ; *Jour. Phys. Chem.*, 1922, **26**, 701, 836 ; 1923, **27**, 376 ; 1924, **28**, 313, 457 ; 1925, **29**, 435, 659 ; 1926, **30**, 628, 830 ; *Koll. Zeit.*, 1923, **33**, 18, 29, 193 ; 1924, **34**, 262 ; 1924, **35**, 144 ; 1925, **36**, 129.

(4) It has been shown that the large amount of adsorption of ions associated with the coagulation of sols like MnO_2, $Fe(OH)_3$, $Al(OH)_3$ $Cr(OH)_3$ etc., is mainly due to the marked chemical affinity of these substances for the coagulating ions.

It is of interest to note that those substances, which can form complex salts with the adsorbent are adsorbed most.

It appears that hydrated MnO_2, which behaves like H_2MnO_3 and hydrated SiO_2, which behaves like H_2SiO_3, can adsorb large quantities of OH' ions, because an acidic substance has naturally a great affinity for OH' ions.

It has been proved (Dhar, *J. Phys. Chem.*, 1924, **28**, 125) that when an alcoholic solution of iodine is added to starch sol, the electric conductivity of the blue substance formed is much greater than the sum of the conductivities of the individual substances. The product obtained by the adsorption of iodine by starch is appreciably conducting and behaves something like an unstable iodide.

It will be interesting to mention here that Gillespie and Hall (*J. Amer. Chem. Soc.*, 1926, **48**, 1207) and Lambert and Gates (*Proc. Roy. Soc.*, 1925, A **108**, 456) have concluded from their experiments on the adsorption of hydrogen by palladium that definite chemical combination takes place between hydrogen and palladium.

We have observed a peculiar phenomenon, that the adsorption of ions by MnO_2 depends on the total volume of the solution used and for a definite concentration of the electrolyte, increase in the volume of the electrolyte leads to an increment in the amount of adsorption by a definite weight of MnO_2, showing that the simple adsorption isotherm is not obtained with the adsorption by MnO_2.

Evidently the phenomenon of adsorption is most marked when there is chemical affinity between the adsorbent and the substance which is being adsorbed.

Adsorption of ions carrying the same charge as the sol or the suspended solid substance.

We have proved that negatively charged hydrated manganese dioxide, not only adsorbs cations but it also adsorbs appreciable quantities of anions and of OH' ions.

The following results were obtained in the adsorption of acids and bases by hydrated manganese dioxide :—

Electrolyte.	Original concentration of H° or OH′ ion.	Amount of H° or OH′ ion adsorbed.
H_2SO_4	0·0094 gr. of H°	0·0003 gr. H°
CH_3CO_2H	0·0162 ,, ,,	0·0003 gr. H°
NaOH	0·0170 gr. of OH′	0·008 gr. OH′
KOH	0·0170 gr. of OH′	0·008 gr. OH′

The following results were obtained with hydrated silica :—

Electrolyte.	Original concentration.	Percentage of adsorption
CH_3CO_2H	0·0540	0·46
$H_2C_2O_4$	0·0310	0·25
$C_6H_5CO_2H$	0·0145	0·24
H_2SO_4	0·0256	0·51
HCl	0·0298	0·12
HNO_3	0·0322	0·21
NH_4OH	0·00351	29·1
NaOH	0·00564	30·68
$Ca(OH)_2$	0·00059	77·27
$Ba(OH)_2$	0·00768	54·4

The foregoing experiments prove that though hydrated MnO_2 or SiO_2 is negatively charged, more of OH′ ions are adsorbed than H° ions, because of the marked chemical affinity of the acidic substances like MnO_2, SiO_2 etc., for OH′ ions. Here we see that adsorption is influenced more by chemical affinity of the adsorbent for the substance which is being adsorbed than the nature of the electric charge on the adsorbent.

We have also proved that barium sulphate in the course of its precipitation, not only adsorbs negative ions from electrolytes, but it also adsorbs positive ions as the following results will show.

Electrolyte.	Original concentration of positive ion.	Percentage of adsorption.
KCl	0·1038 M	0·1
$K_2C_2O_4$	0·06894 M	2·0
$KBrO_3$	0·09400 M	0·6
Na_3AsO_3	0·08833 M	3·7

We have also observed that Cl′, SO_4″ and C_2O_4″ ions are adsorbed by negatively charged sols of As_2S_3, Sb_2S_3 etc., when they are

*coagulated by KCl, K₂SO₄, K₂C₂O₄ etc. The following quanti-
tative result has been obtained with KCl and As₂S₃ sol :—*

Adsorption of Potassium and Chlorine Ions.

Amount of $As_2S_3 = 0.4508$ gram; volume = 100 c.c.

Original concentration.	Final concentration.	Adsorption.
0·05997 Cl′	0·05900 Cl′	1·6 per cent.
0·05997 K°	0·05790 K°	3·3 ,.

Hence the ratio of the adsorption of potassium ion to chlorine ion in the coagulation of a sol of $As_x S_3$ by KCl is 2·06.

The importance of the adsorption of ions carrying the same charge as the sol will be evident from the following considerations :—

(1) The abnormal dilution effect, shown by sols like As_2S_3, $Sb_2 S_3$, mastic, gum dammar, Prussian blue etc., when coagulated by univalent ions like K°, Na°, Li° etc., (*viz.* more of electrolytes like KCl, NaCl, LiCl etc., are necessary to coagulate a dilute sol than a concentrated one), is mainly due to the fact that these sols can adsorb ions carrying the same charge as the sols.

(2) The abnormal behaviour, shown by sols like As_2S_3, $Sb_2 S_3$, mastic, Prussian blue, etc., when coagulated by mixtures of electrolytes (*i.e.* the precipitation values of mixtures of electrolytes of widely varying precipitating powers are much greater than the additive values), is also due to the adsorption of ions carrying the same charge as the sol.

(3) The phenomenon of positive acclimatization has been explained from the point of view that colloidal particles can adsorb ions carrying the same charge as the sol. It follows, therefore, that such sols as As_2S_3, $Sb_2 S_3$, mastic, etc., which are known to adsorb negative ions show this phenomenon more markedly than sols of $Fe(OH)_3$ $Cr(OH)_3$ etc., which hardly adsorb monovalent ions carrying the same charge as the sols.

(4) Moreover, we have proved that when small quantities of electrolytes insufficient to coagulate the sols are added to them, the sols adsorb ions carrying the same charge as the sol and their stability is increased due to the increase in their charge and the viscosity is slightly decreased.

Consequently we are of the opinion that the above four phenomena,—(*a*) abnormality of sols to follow the general dilution rule,

(b) the abnormal behaviour of sols towards a mixture of electrolytes of widely varying precipitating powers, (c) the phenomenon of positive acclimatization and (d) the decrease of viscosity of sols on the addition of small quantities of electrolytes, are essentially connected and go hand in hand and are mainly due to the adsorption of ions carrying the same charge as the sol. We have observed that the above generalisation is applicable to sols of $Fe(OH)_3$ (negatively charged and positively charged), $Cr(OH)_3$ (negatively charged and positively charged), $Al(OH)_3$, MnO_2 (negative and positive), $Sn(OH)_4$ (negative and positive), Prussian blue, uranium ferrocyanide, thorium hydroxide, mastic, gum dammar, As_2S_3, Sb_2S_3, sulphur, gold, silver, V_2O_5, etc. Moreover we have proved that when positively charged ferric hydroxide is coagulated by KCl, K_2SO_4, K_2HPO_4 etc., no abnormality is obtained, but when the above sol is coagulated by $FeCl_3$ or $Al(NO_3)_3$, the sol behaves abnormally towards dilution, towards a mixture of electrolytes, shows the phenomenon of positive acclimatization markedly and shows decrease of viscosity on the addition of small quantities of $FeCl_3$ (compare the measurements of Thomas and Frieden, *J. Am. Chem. Soc.*, 1923, **45**, 2522, on the viscosity of $Fe(OH)_3$ sol in presence of $FeCl_3$) ; because $Fe^{\cdots}$ or $Al^{\cdots}$ ions are adsorbed by a positively charged sol of $Fe(OH)_3$.

Experimental results on the viscosity measurements of colloids, specially of the hydrophobe type, are in support of the following assumptions :—

(1) Other things being equal, the uncharged substance is more hydrated than the sol.

(2) The greater the hydration of a substance, the greater is its viscosity.

(3) When a sol adsorbs an ion carrying the same charge as the sol due to chemical affinity and thus the charge on the sol is increased, we always observe a decrease in the viscosity of the sol.

(4) When the sol adsorbs more of the ion carrying the opposite charge than the ion carrying the same charge, the charge on the sol is decreased and more of hydration will take place and the viscosity will be increased (compare Dhar, *J. Chem. Soc.*, 1925, **129**, 1556; *Zeit. Elektrochem.*, 1925, **31**, 261; Chakravarti and Dhar, *Zeit. anorg. Chem.*, 1926, **152**, 393).

Our experimental results on the viscosity of various sols in presence of small quantities of electrolytes are in opposition to the view that the sol is more hydrated than the coagulated

mass and that greater the charge on a particle, the greater the hydration.

Adsorption of Sols by their own Precipitates.

We have made quantitative experiments on the adsorption of sols by their own freshly obtained precipitates, free from all electrolytes. We have observed that many sols are copiously adsorbed by the solid precipitates of the same substances.

(a) Adsorption of a sol of silver chromate by freshly precipitated silver chromate.

A sol of silver chromate was prepared by adding a dilute solution of silver nitrate to an equivalent amount of potassium chromate containing gelatine.

Solid silver chromate was obtained by the interaction of silver nitrate and potassium chromate and was thoroughly washed free from electrolytes. The solid silver chromate was suspended in water and known amounts were taken out by means of a pipette after thoroughly shaking the water containing the precipitate. One typical experimental result is given below :—

Weight of Ag_2CrO_4 in 10 c.c. water containing $Ag_2CrO_4 = 1.4680$ g.
Weight of Ag_2CrO_4 in 25 c.c. sol $= 0.0141$ g.
Concentration of gelatine in the sol $= 0.25\%$

Ratio of $\dfrac{Ag_2CrO_4 \text{ precipitate}}{Sol}$ by weight	Percentage of adsorption.
26	32.3
52	43.1
78	56.1
104	66.5
156	73.6
208	81.7
312	90.6

Similar experiments were carried on the adsorption of a sol of $PbCrO_4$ by a precipitate of lead chromate. The sol of lead chromate was obtained by the action of lead acetate on potassium chromate containing agar.

Concentration of agar in the sol $= 0.238\%$
Weight of lead chromate in 10 c.c of
         water containing $PbCrO_4 = 0.7058$ g.

Weight of PbCrO$_4$ per litre of sol = 0·3090 g.

Ratio of $\dfrac{\text{percipitate}}{\text{sol}}$ by weight	Percentage of adsorption.
22·8	63·4
30·4	71·0
45·6	73·0
60·8	74·1
68·4	85·0
91·2	87·0
182·4	89·0

The foregoing experimental results prove that sols of silver chromate, lead chromate, etc., are markedly adsorbed by their solid precipitates. Similarly we have found out that sols of Fe(OH)$_3$, Ni(OH)$_2$, Co(OH)$_2$, HgO, ZnS, As$_2$S$_3$, etc., are adsorbed by their solid precipitates.

On the other hand, sols of Sb$_2$S$_3$, CdS, Ag$_2$S, MnO$_2$ etc., are not adsorbed by their respective solids.

Basing on these experiments we have advanced a theory of the formation of Liesegang rings (*J. Phys. Chem.*, 1924, **28**, 41; *Koll. Zeit.*, 1924, **35**, 270; 1925, **37**, 2, 89). The basic idea of our theory is that Liesegang rings are formed by the coagulation of a peptised sol and that the coagulated mass in the course of its coagulation and when coagulated adsorbs and coagulates completely or partially the sol of the same substance from the neighbouring layers.

If the precipitate is unable to adsorb and coagulate the sol, there would not be any clear space, but bands consisting of alternate layers of different colours will form.

We have proved that there are two distinct classes of Liesegang rings. In one class, two consecutive rings are separated by clear spaces, whilst in the other case, the rings consist of a layer of coagulated sol followed by a layer of the peptised substance.

The theory advanced by us takes into consideration the influence of the gel and assumes that the sparingly soluble substance, *e.g.*, silver chromate formed by diffusing silver nitrate into potassium chromate in gelatine gel, is at first in the colloidal condition due to the peptising influence of the gel. Owing to the high concentration of the diffusing electrolyte at the beginning, the quantity of the sparingly soluble substance formed is much in excess to that which the gel can hold in suspension and thus it coagulates, this process being further facilitated by the other product of the chemical change

(*e.g.*, KNO$_3$ in this case). The advancing layers of the diffusing electrolyte (*e.g.*, AgNO$_3$,) meet fresh quantity of potassium chromate and produce silver chromate at first in the colloidal condition. This sol of silver chromate is gradually adsorbed and coagulated by the solid silver chromate already formed. In this way, a layer next to the solid becomes free from silver chromate sol which removes along with it the chromate ions used in its production. The diffusing silver nitrate passes through this layer, which is practically free from chromate ions and comes in contact with another layer of potassium chromate and at first it forms a layer of colloidal silver chromate, which can no longer be adsorbed and coagulated by the solid silver chromate already formed, as the limit of adsorption has been already reached and this new layer is formed a little too far from the solid silver chromate for the possibility of its being adsorbed by the solid silver chromate. Now the silver nitrate is continually diffusing and gradually the concentration of the silver chromate sol increases and finally the limit to which the gel can hold the silver chromate in suspension is reacted and the silver chromate becomes coagulated. The process repeats itself and we get a series of rings separated by clear spaces practically free from the sparingly soluble substance.

We have proved that a stable yellow negatively charged sol of silver chromate is formed in gelatine by the preferential adsorption of chromate ions, whilst a red unstable sol of positively charged silver chromate is formed by the adsorption of silver ions.

Moreover, our theory is capable of predicting that those freshly obtained precipitates, which are capable of adsorbing their respective sols will form Liesegang rings of the first type in which two consecutive rings will be separated by a clear space, whilst substances which cannot adsorb their respective sols should give Liesegang rings of the second type, which consists of alternate layers of different colours. Experimental results show that Ag$_2$CrO$_4$, PbCrO$_4$, Fe(OH)$_3$ etc., which can adsorb their respective sols form Liesegang rings of the first type, whilst Sb$_2$S$_3$, CdS, MnO$_2$ etc., which cannot adsorb their own sols, form Liesegang rings of the second type in which there are no clear spaces.

We have been able to prove from experiments that our theory stands on a better footing than the theories of Wilhelm Ostwald (*Zeit. physikal Chem.*, 1897, **23**, 365) Bradford (*Biochem. J.*, 1916, **10**, 169; 1917, **14**, 157) and Wolfgang Ostwald (*Koll. Zeit.*, 1925, **36**, 880).

Summary and Conclusion

(1) Experiments on the adsorption of ions by sols of HgS, Sb_2S_3, $Al(OH)_3$, $Fe(OH)_3$, V_2O_5, MnO_2 etc., show that the greater the valency of an ion, the less is the amount of adsorption. There is no experimental support for the assumption that the greater the valency and hence the coagulating power of an ion, the greater is its adsorption.

(2) The phenomenon of adsorption is most marked when there is chemical affinity between the adsorbent and the substance which is being adsorbed.

(3) Experimental results show that sols are capable of adsorbing ions carrying the same charge as the sol.

(4) The abnormality of sols to follow the general dilution rule, the abnormal behaviour of sols towards a mixture of electrolytes, the phenomenon of positive acclimatization and the decrease of viscosity of sols on the addition of small quantities of electrolytes, are essentially connected and are mainly due to the adsorption of ions carrying the same charge as the sol.

(5) Experiments on viscosity of sols in presence of electrolytes show that other things being identical, an increase in the charge of the sol produces a decrease in the viscosity and hydration of the sol.

(6) Sols of silver chromate, lead chromate, ferric hydroxide, etc., are copiously adsorbed by their respective solids. On the other hand, sols of antimony sulphide, cadmium sulphide, manganese dioxide etc., are not adsorbed by their solid substances. Basing on these observations, a theory of the formation of Liesegang rings in which a layer of precipitate is followed by a clear space, has been advanced.

Action of Hydrazides. Part I. Synthesis of Triazines from Aminoguanidine and Diketones.

By Satish Chandra De.

Semicarbazide reacts with most diketones so as to yield semi-carbazones (Bromberg, *Ber.*, 1897, **30**, 132; Thiele and Barlow, *Annalen*, 1898, **302**, 323; Schmidt and Sauer, *Ber.*, 1911, **44**, 276, 3250). With benzil, however, it forms a triazine derivative (Thiele and Stanger, *Annalen*, 1894, **283**, 20).

In a study of the reaction between aminoguanidine and a-dike-tones, Thiele and Bihan (*Annalen*, 1898, **302**, 307) found that the aliptiatic a-diketones yield osazones, whilst benzil yields a derivative of triazine, thus:—
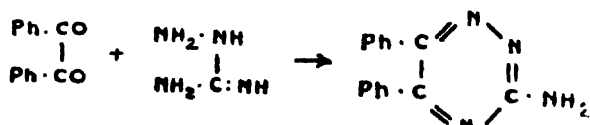
The author has studied further the reaction between aminoguani-dine and aromatic diketones, and as a result derivatives of triazine have been obtained.

The behaviour of semicarbazide towards diketones is thus different from that of aminoguanidine. The most reasonable ex-planation for the tendency of aminoguanidine to form a ring system is, perhaps, its stronger basic character. In semicarbazide, NH_2.NH. CO. NH_2, which is the amide of hydrazocarbonic acid, NH_2.NH. $COOH$, the amino part of the group ($-CO.NH_2$) is acidic in its nature. When the hydrazine residue combines with a ketonic group in a diketone so as to form a semicarbazone, the acidity of the amino group is enhanced, and this group is prevented from reacting with the remaining ketonic group, which also is acidic in nature. It would seem that a triazine might be formed, but it is not, by the elimination of a molecule of water from the semicarbazone. The triazine is formed, however, from the semicarbazone monoxime in

which the acidity of the —CO group has been reduced by conversion
into —C:NOH.

$$-C = N - NH \qquad -C:N \cdot NH \quad -C = N - NH$$

$$-\overset{\cdot}{C} \mid O\ H_2\ \overset{|}{N} \cdot \overset{\cdot}{C}O \qquad -\overset{\cdot}{C}:N \cdot \overset{\cdot}{C}O \quad -\overset{\cdot}{C} = NOH\ H_2\ N \cdot \overset{|}{C}O$$
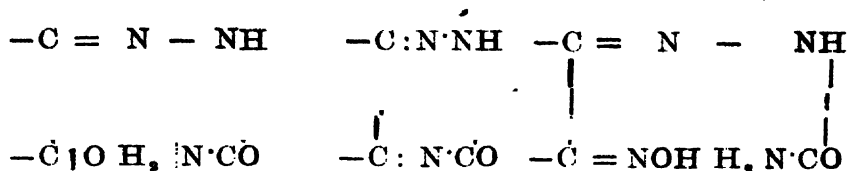
Aminoguanidine differs from semicarbazide in having an imino
group in place of the oxygen atom of the —CO group. Owing to
the imino group, the amino group in the amidine residue, H_2N-
$C=NH$, is basic, accordingly a hydrazone, formed by the con-
densation of aminoguanidine with a diketone, can part with a mole-
cule of water and yield a triazine.

Thiele and Bihan (*loc. cit.*) have described a hydrazone derived
from β-naphthoquinone and aminoguanidine, which with alkali gives
β-naphthol and a compound, $C_{11}H_7N_3O$.

$$= N \cdot NH\ C\left(:NH\right) \cdot NH_2 \qquad = \beta\text{-Naphthol} + C_{11}H_7N_3O$$
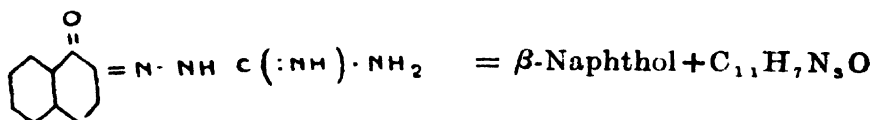
On repeating their process the author has not found it possible to
isolate the hydrazone. Thiele has not given the constitution of the
compound, $C_{11}H_7N_3O$. From the behaviour of diphenylaminotria-
zine, phenanthro-aminotriazine and naphtho-aminotriazine it appears
to the present author that under the influence of alkali a portion of
the hydrazone decomposes giving β-naphthol, while another portion
loses a molecule of water forming a naphtho-aminotriazine, the
amino group of which is then replaced by a hydroxyl group forming a
naphthohydroxytriazine. This view finds experimental support in
that naphtho-aminotriazine has been prepared and converted into
the above naphthohydroxytriazine.

The colour of the triazines obtained from aminoguanidine with
benzil, phenanthraquinone, acenaphthenequinone and isatin is yellow
and that with β-naphthoquinone red. Contrary to expectation
the colour of the triazines in the phenanthraquinone series could not
be deepened by introducing bromine or the nitro group. The colour
of the triazines is diminished by acetylation.

EXPERIMENTAL.

5 : 6-Acenaphtho-3-aminotriazine.
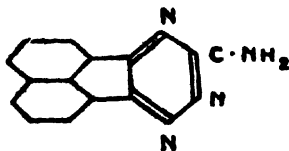
To acenaphthenequinone in hot acetic acid solution, was added the requisite quantity of aminoguanidine hydrochloride and the mixture boiled for three hours.   The aminotriazine was precipitated with ammonia as a yellowish brown flocculent precipitate which after crystallisation from pyridine was obtained in deep yellow shining plates, m. p. above 305°.   It is insoluble in water, benzene, ether and alcohol. (Found : N, 25·63. $C_{13}H_8N_4$ requires N, 25·45 per cent.).

The *acetyl* derivative crystallised from alcohol in feebly yellow needles, m.p. 268°. (Found : N, 21·61. $C_{15}H_{10}ON_4$ requires N, 21·37 per cent.).

5 : 6-Naphtho-3-aminotriazine.
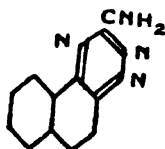
β-Naphthoquinone and aminoguanidine hydrochloride in acetic acid solution were heated for four hours after which the triazine was precipitated with ammonia as a red amorphous powder.   This was collected and crystallised from pyridine in reddish yellow microscopic needles, m. p. 240°.   It is insoluble in water, benzene, and ether; very slightly soluble in alcohol. (Found : N, 28·80. $C_{11}H_8N_4$ requires N, 28·57 per cent.).

The *acetyl* derivative was obtained as a dirty white precipitate, m.p. 208°, insoluble in ordinary organic solvents.   (Found : N, 23·32. $C_{13}H_{10}ON_4$ requires N, 23·53 per cent.).

5 : 6-Naphtho-3-hydroxytriazine.

It was obtained from aminonaphthotriazine with strong potassium hydroxide solution.   As the triazine decomposed it gradually went

into solution and after several hours' heating, a small quantity of a yellow precipitate separated which, however, dissolved in the alkaline solution on dilution with water. From this solution the free base was precipitated with acid as a yellow powder which crystallised from alcohol in yellow micro-crystalline powder. It dissolves in alcohol with a red colour and green fluorescence. It is insoluble in benzene, chloroform and ether; soluble in alcohol and and acetic acid. (Found: N, 21·45. $C_{11}H_7ON_3$ requires N, 21·32 per cent.). Thiele and Barlow (loc. cit.) probably obtained this compound by heating β-naphthoquinone aminoguanidine with a concentrated aqueous solution of alkali and the pronounced acid character of the substance, noticed by them, is due to the presence of a phenolic group in the molecule.

5 : 6-*Isato-3-aminotriazine*.
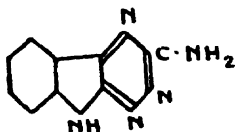
Molecular quantities of isatin and aminoguanidine hydrochloride were heated in acetic acid solution. At first the solution was red and as the reaction proceeded it assumed an orange colour and after a few minutes long needles of the hydrochloride of amino-isato-triazine began to separate. After an hour the mixture was allowed to cool when a further quantity of crystals was deposited. The hydrochloride was dissolved in water and the triazine precipitated with ammonia as yellow needles. Crystallised from alcohol in yellow needles it turned brown at 200° and did not melt at 296°. (Found : N, 37·99. $C_9H_7N_5$ requires N, 37·84 per cent.).

The *acetyl* derivative separated from alcohol in light yellow microscopic crystals, m.p. 200°. (Found : N, 25·85. $C_{13}H_{11}O_3N_5$ requires N, 26·02 per cent.).

5 : 6-*Bromophenanthro-3-aminotriazine*.

It was obtained from 2-bromophenanthraquinone and aminoguanidine hydrochloride in acetic acid solution; precipitating with ammonia. Crystallised from alcohol it was obtained in reddish yellow needles, m.p. 235°. It is insoluble in benzene and chloroform;

soluble in acetic acid and pyridine. (Found : N, 17·59. $C_{18}H_9N_4Br$ requires N, 17·23 per cent.).

The *acetyl* derivative was purified by crystallisation from pyridine from which it separated in light yellow microscopic crystals, m.p. 278°. (Found : N, 15·48. $C_{17}H_{11}ON_4Br$ requires N, 15·26 per cent.).

5 : 6-*Dibromophenanthro-3-aminotriazine*, prepared from 4 : 5-di-bromophenanthraquinone and aminoguanidine hydrochloride as described before, crystallised from pyridine in greenish yellow plates which did not melt at 305°. It is insoluble in alcohol, benzene and chloroform; very sparingly soluble in acetic acid. (Found : N, 14·13. $C_{16}H_8N_4Br_2$ requires N, 13·86 per cent.).

The *acetyl* derivative crystallised from nitrobenzene in light yellow rectangles not melting at 310°. It is insoluble in alcohol, benzene, acetic acid and pyridine. (Found : N, 12·68. $C_{17}H_{10}ON_4Br_2$ requires N, 12·56 per cent.).

5 : 6-*Dibromo-phenanthro-3-aminotriazine*.—It was prepared from 2 : 7-dibromophenanthraquinone and aminoguanidine hydrochloride by methods already described. The precipitate that separated was collected and crystallised from pyridine when it formed orange coloured rectangles, m.p. 288°. It is insoluble in alcohol, benzene and chloroform; very slightly soluble in acetic acid but readily in hot pyridine. (Found : N, 14·08. $C_{15}H_8N_4Br_2$ requires N, 13·86 per cent.).

5 : 6-*Nitrophenanthro-3-aminotriazine*.—2-Nitrophenanthraquinone and aminoguanidine hydrochloride were heated in acetic acid solution as before and the triazine was precipitated with ammonia. This was collected and crystallised from pyridine yellow needles with a greenish tinge, m.p. 280°. It is insoluble in alcohol, chloroform and benzene and almost insoluble in acetic acid. (Found : N, 24·37. $C_{15}H_9O_2N_5$ requires N, 24·05 per cent.).

The *acetyl* derivative crystallised from pyridine in light yellow needles which turned brown at 280° and melted at 298°. (Found : N, 21·30. $C_{17}H_{11}O_3N_5$ requires N, 21·02 per cent.).

5 : 6-*Nitrophenanthro-3-aminotriazine*.—It was prepared from 4-nitrophenanthraquinone and aminoguanidine hydrochloride. The acid solution was diluted with water and the base was precipitated with alkali as a yellow crystalline mass. This was obtained pure from acetic acid from which it separated in yellow needles, m. p. 215°. (Found : N, 24·31. $C_{15}H_9O_2N_5$ requires N, 24·05 per cent.).

The *acetyl* derivative crystallised from acetic acid in light yellow rectangles or needles, m.p. 270°. (Found : N, 21·25. $C_{17}H_{11}O_8N_4$ requires N, 21·02 per cent.).

5 : 6-*Dinitrophenanthro*-3-*aminotriazine.* ·It was prepared from 2 : 7-dinitrophenanthraquinone and aminoguanidine hydrochloride in presence of acetic acid. The base precipitated with alkali was purified from nitrobenzene from which it crystallised in needles of brown colour which did not melt at 310°. It is insoluble in alcohol benzene and chloroform; very slightly soluble in pyridine. (Found : N, 25·25. $C_{15}H_8O_4N_6$ requires N, 25·0 per cent.).

The *acetyl* derivative crystallised from pyridine in light yellow needles which did not melt at 310°. (Found : N, 22·46. $C_{17}H_{10}O_5N_6$ requires N, 22·22 per cent.).

5 : 6-*Dinitrophenanthro*-3-*aminotriazine.*—It was obtained from 4 : 5-dinitrophenanthraquinone and aminoguanidine hydrochloride in acetic acid solution. The dirty yellow precipitate was purified by crystallisation from pyridine in greenish yellow needles, m.p. 265°. It is insoluble in benzene, chloroform, alcohol and acetic acid; soluble in pyridine and nitrobenzene. (Found : N, 25·38. $C_{15}H_8O_4N_6$ requires N, 25·00 per cent.).

The *acetyl* derivative crystallised from pyridine in straw yellow rectangles, m.p. 275°. (Found : N, 22·28. $C_{17}H_{10}O_5N_6$ requires N, 22·22 per cent.).

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6-Hydroxyquinolyl-5-β-acrylic Acids (*cis-* and *trans-*) and their Derivatives.

By BIMAN BIHARI DEY AND TIRUVENKATA RAJENDRA SESHADRI.

Quinolino-6:5-α-pyrones (*J. Indian Chem. Soc.*, 1926, **3**, 187; also *J. Chem. Soc.*, 1919, **115**, 531), when freshly precipitated from an acid solution, dissolve in a dilute solution of alkali to a considerable extent in the cold, but when recrystallised are insoluble except on heating. The difference is explained by the fact that a freshly prepared quinolino-pyrone is accompanied by the acid that is formed by the rupture of the pyrone ring: the acid, however, is unstable and changes into the quinolino-pyrone on treatment with a hot solvent.

These acids have now been isolated in the pure condition in the form of pale yellow crystalline powders. They rapidly lose water and form pyrones even at the laboratory temperature: their silver salts can be preserved unchanged for a longer time if kept in desiccators of non-actinic glass. They should obviously be regarded as *cis*-6-hydroxyquinolyl-5-β-acrylic acids. The relation between the quinolino-pyrone and the acrylic acid is shown below :—
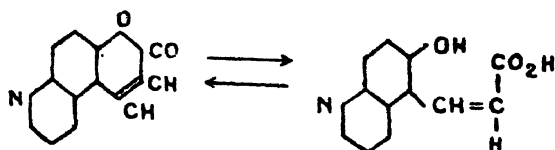
The *cis*-isomers being too unstable to work with, attention was directed to the preparation of the *trans*-isomers by the methods generally employed for converting coumarins into coumaric or *trans*-hydroxycinnamic acids, *i.e.*, by heating with concentrated alkali or sodium ethoxide in alcoholic solution for several hours, or by fusion with potash at 250°—300° for a shorter time. These methods, however, did not lead to the desired result, only the unchanged pyrones being obtained at the end of the operation. Coumarin itself yields, under the same conditions, first coumaric and subsequently salicylic acid.

The basic quinoline ring appears, therefore, to confer stability on the pyrone nucleus. Similar observations have been recorded in the case of some amino-coumarins (Pechmann, *Ber.*, 1899, **32**, 3684) and nitro-coumarins (Dey and Row, *J. Chem. Soc.*, 1924, **125**, 555) which are unaffected by boiling alkalis or sodium alcoholates, whilst 8-nitro-coumarin provides one of the few instances of a coumarin yielding a stable coumarinic acid. These examples seem to point to the existence of a remarkable influence of either acidic or basic groups in stabilizing the coumarinic, *i.e.*, the *cis*-phase, so that the ordinary methods are of no avail in converting them into the corresponding coumaric or *trans*-acids.

The new method recently developed in this laboratory (*cf.* Dey and Row, *J. Chem. Soc.*, 1924, **125**, 554) was therefore tried, and it was found that on boiling the quinolino-pyrones successively with sodium sulphite and concentrated alkali solutions, they were completely converted into the salts of the *trans*-acids. The change is represented as taking place in the following way :—
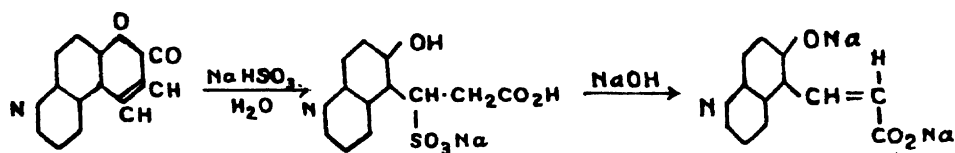
The *trans*-hydroxyquinolyl acrylic acids are stable substances, soluble both in acids and alkalis, but dissolving with great difficulty in the ordinary organic solvents. They are quantitatively transformed into the quinolino-pyrones on warming with concentrated sulphuric acid on the water-bath, and they decompose vigorously at their melting points into carbon dioxide and the corresponding hydroxy-quinolyl-ethylenes. These reactions, which are parallel to the changes undergone by coumaric acid itself under the same conditions, as well as their mode of preparation, furnish definite evidence of the *trans*-structure of the acids. The curious observation, however, was made that the ethyl esters of the *trans*-acids possess the remarkable property, verified in several cases in the course of these investigations, of eliminating alcohol when heated above their melting points and passing into the quinolino-pyrones.

The acids and their esters, therefore, behave differently when heated, the former like other *trans*-acids of this series losing carbon dioxide and passing into styrene derivatives, whilst the latter split off

ethyl alcohol and form quinolino-pyrones, as if they had the *cis*-configuration. The presumption that the acids had undergone a change in configuration during the process of esterification seems to be untenable, because the esters, on keeping in contact with cold alcoholic potash, were found to be hydrolysed to the original *trans*-acids. The various changes are shown in the scheme given below :—
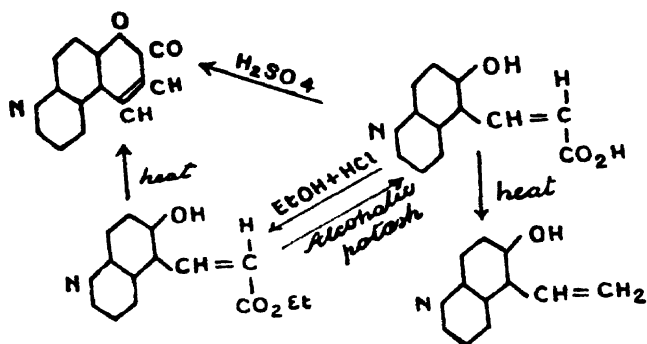
There are many cases on record in which the elimination of atoms or groups takes place very readily from the *trans*-position; thus, the *trans*-forms of β-chlorocrotonic acid, bromo-stilbene and bromo-butylene lose halogen acid with ease, although the corresponding *cis*-derivatives do not (*cf.* Frankland, *J. Chem. Soc.*, 1912. **101**, 681).

The hydroxyquinolyl ethylenes are colourless solids, melting at high temperatures; they readily dissolve in dilute caustic soda and in dilute hydrochloric acid to form colourless solutions which soon deposit the sparingly soluble sodium salt or the hydrochloride. Neutral ferric chloride develops a fine pink colour, indicating the presence of a phenolic group.

EXPERIMENTAL.

ACTION OF ALKALI ON QUINOLINO-PYRONES.

cis-6-*Hydroxyquinolyl-5-β-acrylic Acid.*

General Method.

The quinolino-pyrone (2 g.) was dissolved in boiling 10 per cent. potassium hydroxide (20 c.c.) and the yellow solution cooled in ice and carefully neutralised with N-hydrochloric acid, when the

cis-hydroxyquinolyl acrylic acid mixed with some unchanged pyrone was precipitated. The latter was eliminated by treating the product with cold dilute sodium carbonate and neutralising the rapidly filtered solution. On repeating this operation twice, the cis-acid was obtained as a yellow micro-crystalline powder, completely soluble in cold dilute sodium carbonate with a deep yellow colour. The acid could not be preserved unchanged for more than a few hours at the ordinary temperature, and after leaving for a day most of it was found to be insoluble in sodium carbonate having changed into the pyrone. The same ring closure also occurred on attempting to crystallise the acid from low boiling solvents like acetone, chloroform or methyl alcohol.

The *di-silver salt* was obtained by the action of silver nitrate on an aqueous solution of the potassium salt. The latter was produced by dissolving a weighed quantity of the quinolino-pyrone in a known excess of dilute potash (over 2 molecules) and subsequently removing the excess by the addition of the calculated quantity of dilute nitric acid. It separates as a deep yellow, flocculent precipitate and when kept dry slowly turned grey on standing; it regenerated the original quinolino-pyrone, when treated with dilute nitric acid or sulphuretted hydrogen.

cis-6-*Hydroxyquinolyl*-5-β-*acrylic* *Acid*.

It was obtained from quinolino-6:5-a-pyrone as a light yellow powder. It underwent rapid decomposition at about 130' and changed into the original pyrone melting at 231-232². The *silver salt* was analysed. (Found: Ag, 50·2. $C_{1s}H_7O_sNAg_s$ requires Ag, 50·4 per cent.).

cis-2-*Methyl*-6-*hydroxyquinolyl*-5-β-*acrylic* acid was produced from 2-methylquinolino-6:5-a-pyrone. It decomposed rapidly at about 175° and the product of decomposition was identified with the original pyrone. The *silver salt* was analysed. (Found: Ag, 49·0. $C_{1s}H_9O_sNAg_s$ requires Ag, 48·7 per cent.).

cis-8-*Methyl*-6-*hydroxyquinolyl*-5-β-*acrylic* acid, the product of hydrolysis of 8-methylquinolino-6:5-a-pyrone, is a bright yellow powder decomposing rapidly at about 120°. The orange coloured *silver salt* was analysed. (Found: Ag, 48·3. $C_{1s}H_9O_sNAg_s$ requires Ag, 48·7 per cent.).

Action of Sodium Sulphite and Alkali on Quinolino-pyrones.
trans-*Hydroxyquinolyl acrylic Acids.*

These acids were obtained by the action of sodium sulphite and strong potassium hydroxide solution used successively. The following was the general procedure:—The quinolino-pyrone (4 g.) was treated with an aqueous solution of sodium sulphite (4 g. in 12 c.c. of water) and boiled until the solution gave no precipitate on neutralisation. This usually took about half an hour after which potassium hydroxide (5 g.) was added and the boiling continued for nearly an hour. On cooling the solution, crystals of the sodium salt of the *trans*-acrylic acid were slowly deposited. These were dissolved in water and the filtered solution carefully neutralised, when the free acid was obtained as a pale yellow flocculent precipitate which was collected and washed. It was found to be insoluble in all the common neutral solvents and was therefore purified by dissolving in dilute sodium carbonate solution in the cold and, after filtration, reprecipitating with dilute acids. It was boiled with absolute alcohol which removed the last traces of impurities and left the acid as a fine powder.

trans-6-*Hydroxyquinolyl*-5-β-*acrylic acid* prepared as above from quinolino-6 : 5-a-pyrone is a white powder, m.p. 220° (decomp). (Found : N, 6·7. $C_{12}H_9O_3N$ requires N, 6·5 per cent.).

The acid dissolved readily in cold dilute hydrochloric acid and caustic soda yielding non-fluorescent yellow solutions from which on concentration the *hydrochloride* and the *sodium salt* separated as colourless and light yellow crystals respectively. It forms a bright yellow *silver* salt, a green *copper* salt, a buff coloured *ferric* salt, a yellow *nickel* salt and a brown *lead* salt. The silver salt was obtained by the method already given. It was filtered, washed thoroughly with water and then with alcohol, dried on a porous tile in a vacuum desiccator and analysed. (Found : Ag, 50·1. $C_{12}H_7O_3NAg_2$ requires Ag, 50·4 per cent.).

Conversion of 6-Hydroxyquinolyl-5-β-acrylic Acid into Quinolino-pyrone.

The acid (0·5 g.) was treated with concentrated sulphuric acid (5 c.c.) and the solution heated in a boiling water-bath for an hour. It was then poured into cold water, filtered and the clear solution

treated with a slight excess of ammonia when quinolino-6 : 5-a-pyrone crystallised as fine, colourless needles, m. p. 232°.

Ethyl trans-6-Hydroxyquinolyl-5-β-acrylate.

The acid was made into a thin paste with absolute alcohol. When dry hydrogen chloride gas was passed into the mixture, a clear solution was obtained which was boiled under reflux for 3 hours and cooled : colourless needles of the sparingly soluble ester hydrochloride were formed. The whole was poured into water and the acid was neutralised by sodium bicarbonate. The precipitated ester, when crystallised from dilute alcohol, appeared as tufts of colourless needles, m. p. 198-199° (with vigorous decomposition). (Found : N, 5·7. $C_{14}H_{13}O_3N$ requires N, 5·8 per cent.).

The solid product of decomposition melted at 230-231°; it was extracted with a little boiling alcohol and the crystallised product was identified with quinolino-6 : 5-a-pyrone by a mixed melting point determination.

In order to identify the other products of decomposition, the ester (4 g.) was distilled in a test tube immersed in an oil-bath kept at 200°, and the volatile product which was absorbed in a little cold water was identified as ethyl alcohol by the iodoform test.

Methyl trans-6-*Hydroxyquinolyl*-5-β-*acrylate* was obtained by saturating a methyl alcoholic solution of the hydroxyquinolyl-acrylic acid with hydrogen chloride. Crystallisation from 50 per cent. alcohol gave colourless needles, m. p. 202° (decomp.). (Found : N, 6·1. $C_{13}H_{11}O_3N$ requires N, 6·1 per cent.).

The solid product of decomposition had m. p. 232°.

Decomposition of trans-6-Hydroxyquinolyl-5-β-acrylic Acid into 6-Hydroxyquinolyl-5-β-ethylene.

The *trans*-acid (2 g.) was heated in a 50 c.c. distilling flask in an oil-bath under a pressure of 40 mm. The decomposition commenced at 170° and became fairly energetic at 190-200°; the acid slowly turned grey and colourless glistening needles sublimed. The temperature of the bath was finally raised to 225° when the whole mass quietly melted to a light brown liquid. The complete operation lasted about 2 hours, at the end of which the product was cooled, washed with a little alcohol and crystallised from a mixture

of pyridine and alcohol with the addition of a little animal charcoal to remove colour. Colourless prisms were obtained ; m.p. 256-257°, the yield being 60 per cent. of the theory. (Found : N, 8·4. $C_{11}H_9ON$ requires N, 8·2 per cent.).

The compound imparts a pink colour to ferric chloride solution; it is insoluble in a aqueous sodium carbonate or ammonia, but dissolves readily in aqueous sodium hydroxide yielding an almost colourless solution from which the sparingly soluble *sodium salt* quickly separates. It dissolves in dilute acids to form light green solutions. The sulphate is freely soluble whereas the hydrochloride and the nitrate are sparingly soluble and crystallise as shining colourless plates. Platinic chloride, mercuric chloride and potassium dichromate yield only amorphous precipitates. The pure dry *hydrochloride* was analysed. (Found : Cl, 16·9. $C_{11}H_{10}ONCl$ requires Cl, 17·1 per cent.).

trans-2-*Methyl-6-hydroxyquinolyl-5-β-acrylic Acid.*

This was prepared from 2-methyl-quinolino-6 : 5-α-pyrone by successive treatment with sodium sulphite and caustic potash. When purified by solution in sodium carbonate and reprecipitation and final boiling with alcohol, it forms a light yellow powder, m.p. 193° (decomp.). (Found : N, 6·3 $C_{11}H_{13}NO_3$ requires N, 6·1 per cent.).

The salts of the acid and its behaviour with concentrated sulphuric acid are similar to those of 6-hydroxy-quinolyl-5-acrylic acid. From its solution in concentrated hydrochloric acid light yellow rhombic plates of the *hydrochloride* were obtained. The deep yellow *silver salt* was prepared by the method already given. (Found : Ag, 48·9. $C_{13}H_9O_3NAg_2$ requires Ag, 48·7 per cent.).

The *ethyl ester* of this acid, obtained in the usual way, crystallised from alcohol as colourless, sharp needles, m.p. 146° (decomp.). (Found : N, 5·6. $C_{15}H_{15}O_3N$ requires N, 5·5 per cent.).

The product of decomposition when crystallised from alcohol, was identified with 2-methylquinolino-6 : 5-α-pyrone, m.p. 219-220°.

2-*Methyl-6-hydroxyquinolyl-5-β-ethylene.*

The decomposition of 2-methyl-6-hydroxyquinolyl-5-β-acrylic acid was effected in the same way as before. There was perceptible decomposition even at 150°; the temperature was slowly raised to 200° when the whole appeared as a light brown glassy mass. The

product was converted into the sparingly soluble hydrochloride and the crystals filtered and decomposed with ammonia. The free base separated from boiling alcohol in small colourless prisms, m. p. 241-242°. (Found: N, 7·7. $C_{12}H_{11}ON$ requires N, 7·6 per cent.).

It resembles the parent substance in all its properties and forms a sparingly soluble sodium salt and a hydrochloride and nitrate which readily crystallise from moderately concentrated solutions. The *hydrochloride* was analysed. (Found: Cl, 15·9. $C_{12}H_{12}ONCl$ requires Cl, 16·0 per cent.).

trans-8-*Methyl-6-hydroxyquinolyl-5-β-acrylic Acid*.

This was obtained in the usual manner from 8-methyl-quino-lino-6 : 5-a-pyrone, and purified by conversion into the sparingly soluble hydrochloride which separated, even from dilute solutions, as colourless flat needles, m.p. 235° (decomp.). The free acid was liberated by neutralising the hot aqueous solution of the hydrochloride with ammonia. It crystallised from boiling alcohol, in which it dissolved rather sparingly, as yellow hexagonal plates, m.p. 165° (decomp.). (Found: N, 6·2. $C_{13}H_{11}NO_3$ requires N, 6·1 per cent.). The *silver salt* was obtained as a deep orange precipitate. (Found: Ag, 49·0. $C_{13}H_9O_3NAg_2$ requires Ag, 48·7 per cent.).

The *ethyl ester* crystallises from dilute alcohol as colourless needles melting at 165-166° with loss of alcohol and the formation of 8-methyl-quinolino-6 : 5-a-pyrone. (Found: N, 5·4. $C_{15}H_{15}O_3N$ requires N, 5·5 per cent.).

8-*Methyl-6-hydroxyquinolyl-5-β-ethylene*.

The decomposition of 8-methyl-6-hydroxyquinolyl-5-β-acrylic acid was effected under a pressure of 50-60 mm. between 170° and 205°. The grey coloured product was washed with cold alcohol in order to remove impurities and finally crystallised from pyridine when it appeared as colourless rectangular plates, m.p. 244-245°. (Found: N, 7·8. $C_{12}H_{11}ON$ requires N, 7·6 per cent.). The compound is sparingly soluble in ether, chloroform and benzene. It imparts a pink colour to ferric chloride solution and forms a sodium salt and a hydrochloride which are sparingly soluble and crystalline. The *hydrochloride* was analysed. (Found: Cl, 16·2. $C_{12}H_{11}ONCl$ requires Cl, 16·0 per cent.).

The Nitration of Coumarin.

By BIMAN BIHARI DEY AND PANCHAPAKESA KRISHNAMURTHI.

During the nitration of coumarin, by the method described by Morgan (*J. Chem. Soc.*, 1904, **85**, 1233), there was obtained a yellowish, crystalline material which melted indefinitely from 130° to 170°. Attempts were made to isolate a new nitro-derivative from this material but without success. Repeated fractional crystallisation from acetic acid and other solvents led generally to a product melting sharply at 140-141°. This is now found to be a mixture of 6-nitro-coumarin, and another mono-nitrocoumarin.

Each of these nitrocoumarins dissolves in an alkaline solution with the formation of nitro-coumarinates. The free coumarinic acids differ in stability: that derived from 6-nitrocoumarin readily reverts to that substance whilst the other is stable in comparison. A separation was effected on this basis.

On repeatedly dissolving the coumarinic acids in bicarbonate of soda, and fractionally precipitating with dilute acid, an acid was obtained, which, on rapid heating, melted with sudden decomposition at 149°, and gave, on boiling with dilute hydrochloric acid, a nitro-coumarin melting sharply at 187°. On oxidation with permanganate in alkaline solution, it gave 3-nitro-salicylic acid (m.p. 126°) in good quantity, the product being thereby identified with 8-nitro-coumarin (Miller and Kinkelin, *Ber.*, 1889, **22**, 1701).

The direct nitration of coumarin was hitherto supposed to result in the formation of only the 6-nitro-derivative which, on protracted treatment with nitric acid, yielded the 3:6-dinitro- and finally the 3:6:8-trinitro-coumarin. It is now proved that 8-nitro-coumarin, prepared previously by the indirect process from 8-nitro-salicylaldehyde, is also a product of the direct nitration of coumarin and forms approximately 7 per cent. of the total.

The phenomenon of a mixture of two different substances melting sharply appearing to be extraordinary ; the melting points of different mixtures of 6-nitro- and 8-nitro-coumarin were observed. It was found that the mixture in equal amounts melted sharply at 140-141° whilst other mixtures had melted indefinitely.

The product obtained from the residues, melting at 140-141° appears, therefore, to be an equimolecular mixture of the 6-nitro- and 8-nitro-coumarins.

EXPERIMENTAL.

8-*Nitro-coumarin*.

Coumarin (20 g.) was nitrated in the usual way (Morgan, *loc. cit.*), the acetic acid filtrate thrown into water, and the preci pitate collected and washed (6 g.). It was then heated with two per cent. sodium hydroxide solution till the whole of it went into solution with a deep orange-red colour, and cooled to 30°. Very dilute hydrochloric acid was added until the solution was faintly acidic. The bulky yellow precipitate was allowed to stand for about 15 minutes and then collected. (The filtrate, after a short time, gave a quantity of needle-like crystals which were identified as those of 6-nitro-coumarin). The yellow precipitate was kept on porous tile for two hours, and then shaken up with water and excess of sodium bicarbonate. The mixture was filtered. A considerable amount of solid was obtained which proved to be 6-nitro-coumarin. The filtrate was acidified, the coumarinic acids were separated and dried for two hours and dissolved again, in sodium bicarbonate solution. This process of dissolution in bicarbonate and acidification was repeated (usually six times) until the filtrate from the coumarinic acid gave no crystals on standing even for a day. The yellow acid thus obtained when dried, melted with decomposition at 149° if the bath was rapidly heated, and dissolved completely in cold sodium bicarbonate solution even after leaving it on the porous tile for two days. On warming this acid with 4N-hydrochloric acid, a nitro-coumarin, melting at 187°, was obtained. A mixture of this with 6-nitro-coumarin melted indefinitely at 139°-141°.

Oxidation.

The nitro-coumarin obtained above (0·5 g.) was dissolved in 2N-sodium hydroxide (25 c.c.) cooled to 0°, and a 1 per cent. solution of permanganate slowly added. The mixture was finally heated on the water-bath for an hour, the solution filtered from the preci- pitated manganese dioxide, concentrated on the water-bath to a small bulk and acidified with strong hydrochloric acid. Colourless

needles (0·3 g.) separated, m.p. 125-126°, either alone, or mixed with 3-nitro-salicylic acid.

Melting Point of a Mixture of 6-Nitro- and 8-Nitro-coumarin.

The required amounts of the two substances were weighed into an agate mortar, intimately mixed, and the melting point of each mixture was observed thrice.

6-Nitrocoumarin (in gm.)	8-Nitrocoumarin (in gm.)	Approximate temperatures between which complete melting takes place
1	0·25	138°−175°
	0·50	139°−170°
1	0·75	139°−155°
1	1·00	140°−141°
1	1·25	139°−150°
1	1·50	139°−160°
1	1·75	138°−165°
1	2·00	138°−170°

PRESIDENCY COLLEGE,
MADRAS.

Dyes derived from Imidazole-dicarboxylic Acid.

By Jamuna Datt Tewari and Sikhibhushan Dutt.

The present communication is the second* of the series of researches that have been undertaken by the present authors in order to establish that the effect of a doubly linked nitrogen atom in a ring system contained in a dye molecule is not to lighten the colour as found by Ghosh (*J. Chem. Soc.*, 1919, **115**, 1102), but on the contrary to intensify it in most instances. Quantitative measurements of absorption spectra of the various dyes containing doubly linked nitrogen in the ring which are being prepared in this laboratory, and which will be published collectively along with the last paper of the series, tend to show that the effect of a doubly linked nitrogen atom in the ring is to intensify the colour to a certain extent as compared with the corresponding substances containing carbon in place of nitrogen.

With the above object in view, imidazole-dicarboxylic acid has been condensed with various aromatic amino and hydroxy-compounds, and the corresponding dyestuffs obtained. The condensations, as a rule, take place without the use of any condensing agents, but it has been found more suitable to use small quantities of strong sulphuric acid, or tin tetrachloride in most of the cases in order to get better yields of the products. The following substances have been made to condense with imidazole-dicarboxylic acid and the corresponding dyestuffs obtained: phenol, resorcinol, catechol, phloroglucinol, hydroxy-quinol, and *m*-phenylenediamine. In general properties these substances are quite similar to the corresponding phthaleins, but the intensity of colour is slightly greater, and in this respect they are more in accordance with the corresponding quinolineins (Ghosh, *loc. cit.*).

Experimental.

Phenol-imidazomaleein.

$$\begin{matrix} C_8H_2N_2 \\ | \\ CO\text{---}O \end{matrix} > C\,(C_6H_4OH)_2$$

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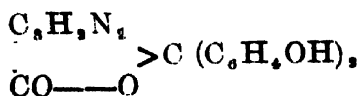
* The first of these papers was published in this *Journal*, 1926, **3**, 161.

A mixture of imidazole-dicarboxylic acid (one mol.), phenol (two mols. plus 20 per cent. excess) and tin tetrachloride (one mol. plus 20 per cent. excess) was heated at 100-110° for about 18 hours. The melt was then poured into water and the excess of phenol distilled off in steam. The residue, after filtration, was extracted with dilute ammonium hydroxide, and the •filtered ammoniacal extract acidified with hydrochloric acid. The precipitated crystalline mass was collected and recrystallised from dilute alcohol in colourless needles, melting at 282°. It dissolves in alkalis with a bright pink colour. (Found : N, 9·49. $C_{17}H_{12}O_4N_2$ requires N, 9·09 per cent.).

Resorcinol-imidazomaleein.

$$\begin{matrix} C_3H_2N_2 \\ | \\ CO \end{matrix} \underset{O}{\overset{}{\rule{1cm}{0.4pt}}} >C< \begin{matrix} C_6H_3\,(OH) \\ \\ C_6H_3\,(OH) \end{matrix} >O$$
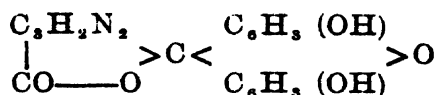
A mixture of imidazole-dicarboxylic acid (one mol.), resorcinol (two mols.) and a few drops of concentrated sulphuric acid was heated at 150-160° for about three hours. The melt was then extracted with dilute sodium hydroxide and the filtered extract ·precipitated with hydrochloric acid. The precipitated dyestuff was then crystallised from a large volume of hot water in yellow needles. When heated the substance blackens at 280-285° and melts with decomposition at 267°. It dissolves in alkalis with an orange-red colour and a fine green fluorescence. (Found : N, 9·02. $C_{17}H_{10}O_6N_2$ requires N, 8·69 per cent.).

Phloroglucinol-imidazomaleein.

$$\begin{matrix} C_3H_2N_2 \\ | \\ CO \end{matrix} \underset{O}{\overset{}{\rule{1cm}{0.4pt}}} >C< \begin{matrix} C_6H_2\,(OH)_2 \\ \\ C_6H_2\,(OH)_2 \end{matrix} >O$$
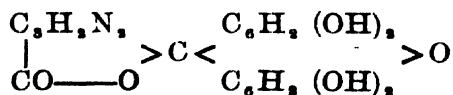
The condensation with phloroglucinol was effected exactly as in the above instance with the difference that the temperature was kept at 200° for about 4 hours. The isolation and purification of the dyestuff were also done in the same manner. The substance crystallises in orange-yellow needles and dissolves in alkalis with

a blood-red colour but without any fluorescence ; m.p. above 290°. (Found: N, 8·2. $C_{17}H_{10}O_7N_2$ requires N, 7·91 per cent.).

Hydroxyquinol-imidazomaleein.

The condensation with hydroxyquinol was effected exactly as in the above two instances with the difference that the temperature was kept at 130-140° for about two hours. The melt was extracted with alcohol and the alcoholic extract, after filtration, cautiously diluted with water, which caused the precipitation of the dyestuff in the form of brownish flocks. It could not be crystallised. It dissolves in alkalis with a bright pink colour and melts with decomposition at 258-260°. (Found: N, 8·1. $C_{17}H_{10}O_7N_2$ requires N, 7·91 per cent.).

Catechol-imidazomaleein.

The condensation with catechol was effected exactly as in the case with phenol. The melt was then thoroughly ground and washed with water acidified with hydrochloric acid. The residue was then extracted with alcohol and the alcoholic extract, after filtration, cautiously diluted with water which caused the precipitation of the dyestuff. It could not be crystallised. It dissolves in alkalis with a transient green colour. (Found: N, 8·82. $C_{17}H_{10}O_5N_2$ requires N, 8·69 per cent.).

m-Phenylenediamine-imidazomaleein.

$$\begin{matrix} C_3H_2N_2 & & C_6H_3(NH_2) \\ | & >C< & >NH \\ CO{-}{-}O & & C_6H_3(NH_2) \end{matrix}$$
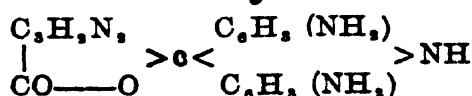
A mixture of imidazole-dicarboxylic acid (one mol.) and m-phenylenediamine hydrochloride (two mols. plus 10 per cent. excess) was cautiously heated in a test tube in the naked flame until the melt assumed a dark red colour. The melt was then allowed to cool and then finely powdered. It was then extracted with absolute alcohol and the alcoholic extract very carefully diluted

with water which slowly deposited the dyestuff in fine brownish yellow needles.   The substance dissolves in alcohol with a bright yellow colour and a green fluorescence.   In dilute acids the colour of the solution is red without any fluorescence ; m.p. above 290°. (Found : N, 22·31. $C_{17}H_{13}O_5N_5$ requires N, 21·94 per cent.).

Jute Seeds—*Corchorus Capsularis.* Part I.

By Nirmal Kumar Sen.

There are two varieties of the jute plant—*Corchorus capsularis* and *Corchorus olitorius*—the seeds of which can be differentiated by their physical appearance. The former are larger in size and of a nut-brown colour, while the latter are of a blue-black colour. *Corchorus capsularis* seeds, procured from the Government Agricultural Farm at Manipur, Dacca, were used in the present investigation.

The seeds are found throughout Bengal. The present price of the seeds is about Rs. 20 per maund. According to Dymock, the seeds possess medicinal properties. In India the seeds, which have a bitter taste, are administered in doses of about 80 grains in cases of fever and obstruction of the abdominal viscera. In spite of these properties it appears that a thorough chemical study of the seeds has not yet been undertaken, though a beginning was made by Kobert (*Ber. Natur. Ges. Rostock; Arch. Freunde Natur. Ges. Mecklenburg,* 1906, *No* 5 ; *vide Chem. Zentr.,* **1907,** I, 1273) and by Tsuno (*Monatsh. pr. Tierheilkunde,* 1895, **6,** 455) who seem to have isolated an impure, amorphous, bitter stuff, under the name of Corchorin, having strongly toxic properties. None of the authors seems to have isolated the oil which is contained in the seed. The present author has therefore undertaken a chemical study of the seeds.

As the seeds when subjected to a high pressure did not yield any oil but were converted into a stiff paste, the powdered seeds were exhaustively extracted with hot petroleum ether in a Soxhlet's apparatus. The residue left after distilling off the petrol was a yellowish brown viscid oil which could not be distilled without decomposition and was free from any readily volatile matter. The oil, which belongs to the class of fixed semi-drying oils, slowly sets to a rubber-like elastic mass in contact with air, but out of contact with it, it can be preserved indefinitely. The oil is free from the bitter taste of the seeds.

After extraction with petroleum ether, the seeds were extracted repeatedly with rectified spirit in a Soxhlet's apparatus. The seeds thus lost their bitter taste. On evaporation of the alcoholic extract

to a small volume and addition of acetone to the solution, a yellow-ish white viscous mass was precipitated : it readily absorbs moisture and turns brown in the air. The substance thus obtained was crystallised from a mixture of glacial acetic acid and acetone as perfectly white crystals which are hygroscopic and readily soluble in water. It tastes somewhat sweet at first, but a bitter after-taste is soon developed. It does not reduce Fehling's solution, but on hydrolysis with dilute mineral acid reduces the solution quite readily even in the cold. In all its chemical properties it corresponds to a glucoside. Besides glucose another substance, insoluble in water, is produced as a product of hydrolysis.

The acetone-alcoholic mother-liquor, on evaporation, yielded another colourless substance which has an extremely bitter taste. It was not obtained in sufficient quantities for investigation but experiments with larger quantities are now in progress. It gives a bluish green colour with concentrated sulphuric acid and does not reduce Fehling's solution. But on hydrolysis with mineral acids an insoluble product is obtained and a sugar which reduces Fehling's solution on heating. From these properties it seems probable that this substance is identical with that with which Kobert worked (*loc. cit.*).

EXPERIMENTAL.

(a) *Characteristics of the Seeds.*

Moisture	7·1 per cent.
Ash (aluminium, potassium and phosphoric acid were detected)	6·0 per cent.
Volatile oil	traces.
Fixed oil (extracted with petroleum ether)	14·78 per cent.

(b) *Characteristics of the Fixed Oil.*

Specific gravity at 28°C	0·921
Viscosity at 28°C	53·1417 relative to water.
Refractive index at 30°·1C ...	1·4705
Optical rotation	0·0
Saponification value	184·4
Iodine value (Wij's method) ...	109·2
Acid value	24·07
Unsaponifiable matter	3·0 per cent.

The solubility and the reactions of the fixed oil are as follows :—
The crude oil was found to be insoluble in water, alcohol, cold glacial acetic acid, dilute sulphuric and nitric acids but readily soluble in ether, benzene, carbon tetrachloride, amyl alcohol and in pyridine. The crude oil was emulsified with sodium carbonate solution and saponified with sodium hydroxide in the cold. Sulphuric acid gives a brown colour which on dilution with water separates a white, gelatinous, light solid. With cold nitric acid part of the oil floats and part goes in solution with a light yellow colour which on dilution with water gives a semi-solid substance. The oil is gradually decolourised by bromine water in the cold and a butter-like substance is produced. With potassium permanganate solution immediate decolourisation takes place in the cold. In the elaïdin test the oil yielded a buttery mass separating from a fluid portion after thirty minutes. Metallic sodium produces a brisk action on the ethereal solution of the oil and a white substance separates.

Extraction of the Seeds with Alcohol.

The seeds after being extracted with hot petrol were extracted with hot alcohol (90 per cent.). The alcoholic solution was filtered and on addition of acetone to the concentrated extract a white gum-like substance separated.

The substance gradually turns brown in air. It contains carbon hydrogen and oxygen only. It dissolves in cold concentrated sulphuric acid with a reddish brown colour : on adding water nothing separates. The substance does not reduce Fehling's solution. Strong hydrochloric acid dissolves it with a port wine colour and the dilute solution reduces Fehling's solution immediately.

It was crystallised from a mixture of glacial acetic acid and acetone in perfectly colourless crystals, which are hygroscopic and readily soluble in water. It is insoluble in acetone, petroleum ether, ethyl ether and absolute alcohol, but soluble in glacial acetic acid and in alcohol (60 per cent.). The substance decolourises potassium permanganate solution. On hydrolysis by dilute mineral acids the substance is decomposed into glucose and another colour-less substance insoluble in water. Evidently the substace is a glucoside. It shrinks at 98° and decomposes with evolution of gas at 105° and shows a dextro rotation of 108°·6 ($[a]_d{}^{2\,0} = +108°·6$). It gives a yellow brown colour with sulphuric acid. This substance is now being further examined. (Found : C, 31·16 ; H, 9·65 per cent.).

Summary and Conclusions.

The oil extracted from the jute seeds with petroleum ether is a non-volatile fixed oil possessing properties very similar to the semi-drying class of oils. It is unsaturated, with a high iodine value, and is readily saponified by caustic alkalis. From the oxidation of the free acids, it seems highly probable that the oil consists of a large proportion of the glycerides of the unsaturated fatty acids such as oleic, linolic and linolenic acids. Further investigation of the oil is now in progress.

Studies in " Photo-sols." Part I.

By S. S. Bhatnagar, N. A. Yajnik and Vasu Dev Zadoo.

Freundlich and Nathansohn (*Koll. Zeit.*, 1921, **29**, 16) while experimenting on the interaction of similarly charged sols, observed the formation of silver sulphide in the reaction between sulphur sol (prepared according to Weirman and Oden) and silver sol (according to Lea's method). In the reaction between arsenic trisulphide sol and silver sol, the formation of a compound of silver, arsenic and sulphur was observed whose composition was not determined. Both reactions were accompanied by a series of characteristic colour changes.

A closer study of the interaction of the arsenic trisulphide sol (prepared according to Lea's method) is made by Freundlich and Moore (*Koll. Zeit.*, 1925, **36**, 17). The reaction taking place in the dark is distinguished from that taking place in light. In dark the original colour of the mixture changes into greenish brown with no further change for weeks over, whereas in light further colour changes ensue and the final colour becomes golden yellow.

The present work is an extension of the above and the authors have tried to investigate how the mixture of arsenic trisulphide sol would behave under different conditions of light, air and concentration with a view to get the mixture which is most sensitive to light and also to find the most effective spectral region. Further the phenomenon of colour changes observed in the interaction of silver sol and antimony trisulphide sol has been studied as also the reaction between gold sol and the two sulphide sols.

Experimental.

Preparation of Sols.

The hydrosol of silver was prepared by Bredig's method using a current of two amperes. Its concentration was determined by Volhard's method. The hydrosols of arsenic and antimony trisulphides were prepared by passing hydrogen sulphide through solutions of arsenious oxide and potassium antimony tartrate respectively and then removing the free hydrogen sulphide by bubbling hydrogen. Their concentrations were determined by coagulating them by dilute

27

hydrochloric acid and weighing the coagulae as trisulphides. The gold sol was prepared by Zsigmondy's method of reducing gold chloride by formaldehyde and also by Bredig's method. The concentration was determined in the latter case by a colorimetric device. The strengths of the different colloidal solutions used in the following experiments are given below :—

Name of the sol.	Weight of the substance per litre.
Ag Sol No. I	0·0995 gms.
Ag Sol No. II (protected in gelatine)	0·3682
Ag Sol No. III	0·1742
Ag Sol No. IV	0·06694
Ag Sol No. V	0·10087
As_2S_3 Sol No. I	1·8440
As_2S_3 Sol No. II	1·980
Sb_2S_3 Sol No. I	0·290
Sb_2S_3 Sol No. II	0·530
Au Sol No. I (Zsigmondy's method)	0·05384
Au Sol No. II (Bredig's method)	0·09423
Au Sol No. III (do)	0·064615

Reaction of the metallic sols with the sulphide sols and the effect of light and air on the interaction.

To study this phenomenon four mixtures having the two ingredients in the same proportion (which is shown in the following tables) were prepared. One was exposed to light only, the second to air only, the third to both light and air and the fourth to neither. Changes of colour in slow stages are observed to take place when the mixtures are exposed to light or to both light and air and no change is undergone in darkness excepting a slight immediate darkening of the colour of the mixture as soon as it is made. It is this darkened colour that is regarded as the initial colour of the mixture in the following tables which show the general results of experiments.

Interaction of Silver Sol and Arsenic Trisulphide Sol.

Constituents of the mixtures.	No. of different sets of mixtures.	Proportion of the two sols in c. cs. in the mixtures.		Colour changes in slow stages when exposed to light or both light and air.		Changes in dark both when exposed to air and when not.
		Ag sol.	As$_2$S$_3$ sol.	Initial colour.	Final colour.	
A. As$_2$S$_3$ sol No. I and Ag sol No. I.	(1)	10	10	Blackish green.	Yellow in 4½ hours.	No change in 24 hours and over two weeks.
	(2)	12	10			
	(3)	10	12			
	(4)	14	9			
B. As$_2$S$_3$ sol No. II and Ag sol No. 1.	Do.	Do.	Do.	Do.	Do.	Do.
C. Ag sol No. II and As$_2$S$_3$ sol No. 1.	(1)	10	10	Dark bluish yellow.	No well marked change in colour in 24 hrs. The mixtures coagulate.	No change excepting coagulation in case of mixtures No. 2 and No. 3 which commenced as soon as they were made.
	(2)	8	10			
	(3)	10	14			
	(4)	8	14			
D. Ag sol No. II and As$_2$S$_3$ sol No. II.	Do.	Do.	Do.	Do.	Do.	

Qualitative Chemical Analysis.

This was done in case of those mixtures which underwent a colour change in light. The method followed in this and the following cases was to coagulate the colloidal particles in the final mixtures by exhaustive cataphoresis. The clear solution and the precipitate thus formed were separated from each other and each examined by the usual analytical methods.

In the present case the investigation consisted in finding as to what new compound or compounds were formed whose constituents would be two or more from among As, Ag, S, and O—the elements participating in the reaction.

Formation of arsenious acid was detected in the clear liquid and of silver sulphide and free sulphur in the precipitate.

Interaction of Silver Sol and Antimony Trisulphide Sol.

Constituents of the mixtures.	No. of different sets of mixtures.	Proportion of the two sols in c. cs. in the mixtures.		Colour changes in slow stages when exposed to light or both light and air.		Changes in darkness whether exposed to air or not .
		Sb_2S_3 sol.	Ag sol.	Initial colour.	Final colour.	
A. Ag sol No. I and Sb_2S_3 sol No. I.	(1)	10	10	Dark with a shade of orange red.	Orange red in 7 hrs.	No change.
	(2)	12	10			
	(·)	10	12			
	(4)	9	14			
B. Ag sol No. V and Sb_2S_3 sol No. I.	Do.	Do.	Do.	Do.	Orange red in 12 hrs.	Do.
C. Ag sol No. II and Sb_2S_3 sol No. I.	Do.	Do.	Do.	No well-marked change. The initial blackishness undergoes a slight decrease.		No change.
D. Ag Sol No. II and Sb_2S_3 sol No. II.	Do.	Do.	Do.	The initial colour of the mixtures darkens a little. There is a tendency towards coagulation which increases with the increase of Sb_2S_3 sol in the mixture.		No change except that mixture No. III coagulates.

Qualitative chemical analysis was done in case of the final mixtures in the combinations of those sols that exhibited a characteristic colour change (in A and B).

Formation of antimonious acid, silver sulphide and free sulphur was detected.

Interaction of Gold Sols and Arsenic Trisulphide Sol.

Preliminary experiments showed that there was little effect of diffused light on the mixture of the above two sols. Sunlight however had an appreciable effect. Exposure to light in the following tables stands for exposure to sun-light.

Constituents of the mixtures.	No. of different sets of mixtures.	Proportion of the two sols in c.cs. in the mixtures.		Colour changes when exposed to light and when to both light and air.		Changes in darkness when exposed to air and when not.
		Au sol.	As_2S_3 sol.	Initial colour.	Final colour.	
A. Au sol No. II and As_2S_3 sol No. I.	(1)	10	10	Green	Yellow-green.	
	(2)	10	6·3	Green with a slight dark shade.	Violet with a greenish yellow shade.	No change.
	(3)	6·3	10	Yellowish green.	Yellow with greenish shade.	
	(4)	16	7	Dark green.	Violet.	
B. Au sol No. II and As_2S_3 sol No. I.	(1)	12	12	The initial colour is bluish green or blue according as the proportion of Au sol is less or more than As_2S_3 sol and the final colour is accordingly blue or indigo after an exposure of 14 hours.		Do.
	(2)	12	8			
	(3)	8	12			
	(4)	16	12			
C. Au sol No. II and As_2S_3 sol No. I.	Do.	Do.	Do.	Do.	Do.	Do.

Note :—The final colours are acquired by the mixtures in A above in 7 hours.

Qualitative chemical analysis of the final mixtures was done in the same way as in the previous cases. Formation of gold sulphide, free sulphur and arsenious acid was detected.

The colour changes accompanying the interaction of Au sol No. II and As_2S_3 sol No. I and Au sol No. II and As_2S_3 sol No. II were observed at intervals by means of Nutting's spectro-photometer. The general result in both cases was that the absorption capacity for light of all sets of mixtures became less and less with the increase in the exposure to light.

Interaction of Gold Sol and Antimony Trisulphide.

Constituents of the mixtures.	No. of different sets of mixtures.	Proportion of the two in the mixture in c.cs.		Changes of colour in slow stages when exposed to light only and when to both light and air.		Time to acquire the final colour.
		Au sol.	Sb_2S_3 sol.	Initial colour.	Final colour.	
A. Au sol No. I and Sb_2S_3 sol No. II.	(1)	10	10	Darkish orange.	Brownish orange.	
	(2)	12	6	Darkish orange.	Orange with violet shade.	6 hours.
	(3)	6	12	Dark.	Orange.	
	(4)	18	6	Dark orange.	Violet brown.	
B. Au sol No. II and Sb_2S_3 sol No. I.	(1)	12	12	Blackish orange.	Black.	
	(2)	12	7	Do.	Blackish blue.	
	(3)	7	12	Orange slightly black.	Brownish black.	14 hours.
	(4)	16	8	Orange black.	Black with a faint blue shade.	
C. Au sol No. II and Sb_2S_3 sol No. II.	Do.	Do.	Do.	Do.	Do.	Do.

As usual no change of colour was noticed in case of mixtures placed in dark.

Qualitative analysis conducted in the same way as before showed the formation of antimonious acid, free sulphur and gold sulphide.

Interaction of Sb_2S_3 sol No. I and Au sol No. III and of Au sol No. III and Sb_2S_3 sol II was followed at intervals by noting the colour changes by means of Nutting's spectro-photometer. The general changes in both cases was the increase in transparency of the mixture with the increase of exposure.

Conclusion.

The photo-sensitive nature of the reaction between silver sol (prepared by Lea's method) was discovered by Freundlich and Nathansohn. The foregoing experiments lead us to conclude that no alteration in this respect takes place in the behaviour of the silver sol, if prepared by Bredig's method. Further we are in a position to say that the reaction between the silver sol and the antimony trisulphide sol is likewise photo-chemical, though slower, so far as colour changes are concerned.

As mentioned in the introduction, the mixture of gold sol and arsenic trisulphide sol was regarded by Freundlich and Nathansohn as indifferent towards light. The present work corroborates this observation with respect to the effect of diffused light, with this addition that the mixture is influenced by the light of the sun, and the interaction in sunlight is also accompained by colour changes. The interaction between gold sol and antimony trisulphide sol is also discovered to be photo-chemical and likewise attended by changes of colour.

Chemical examination of the mixtures when they had attained the final colour reveals the formation of the sulphide of the metal, free sulphur and antimonious or arsenious acid (according as antimony trisulphide or arsenic trisulphide sol was used).

Theory of the Change.

Initially we had the mixture of the metal sol (Ag or Au) and the sulphide sol (As_2S_3 or Sb_2S_3) and after exposure when there was no further change of colour in light, presence of the metal sulphide, free sulphur and the acid (arsenious or antimonious) was detected in the mixture. The change can be explained by considering the sulphide sol to hydrolyse into the acid and H_2S. H_2S can yield

H$_2$O and S by the action of air and light. This accounts for the presence of free sulphur. H$_2$S may react with the colloidal particles of the metal to form its sulphide. The several stages or the different extents to which the reactions proceed would correspond to different states of colour exhibited by the mixture.

Svedberg and other workers in their recent photographic investigations on the nature of " latent image " (*cf*. " Photo-electricity " by Stanley, Ed. 1925. pp. 256-257) postulate the existence of certain sensitization centres in the grain of the photographic film ; again F. C. Toy assumes that such centres are particles which are not silver halide. Further Henry and Sheppard account for the high sensitivity of the film by the presence of nuclei of Ag$_2$S, which according to them contaminate it. Theories regarding the sensitizing action of silver sulphide differ (*vide Journal of the Society of Chemical Industry*, Supplement, March, 1926, p. 219). These theories have direct bearing on our subject. We can likewise postulate that the small quantities of the metal sulphide formed initially in the mixtures of the sols form the centres of photo-chemical sensitivity and accelerate the chemical changes which are accompanied by the corresponding manifestations of colour.

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The Kinetics of the Intramolecular Transformation of Ammonium Thiocyanate to Thiourea and Thiourea to Ammonium Thiocyanate.

By A. N. Kappanna.

The decomposition of nitrogen pentoxide in the gaseous state has now been proved to be a perfectly homogeneous unimolecular reaction. The existence of unimolecular reactions in liquids has been doubted on the grounds that very little is known about the liquid state of matter which is very complex and that molecules in liquids are very much subject to attractions by neighbouring molecules. But, whether or not real unimolecular reactions can exist in liquids should be decided only by experimental study. Lueck (*J. Amer. Chem. Soc.*, 1922, **44**, 757) has found that the decomposition of nitrogen pentoxide dissolved in carbon tetrachloride and chloroform proceeds with almost the same velocity as in the pure gaseous state and that the influence of solvent in this particular case is very small. This would mean that unimolecular reactions may well take place even in solution. The recent work of Watson (*Proc. Roy. Soc.*, 1925, **408**, 132) on the decomposition of derivatives of oxalacetic ester again lends support to the view that reactions of the first order may be met with in pure liquids. The present work was undertaken to see how far an isomeric transformation which takes place in the pure liquid state can conform to the ideal of a unimolecular reaction.

Waddell (*J. Phys. Chem.*, 1898, **2**, 536) first investigated the kinetics of the transformation of ammonium thiocyanate to thiourea and showed in an approximate way that it was a reversible reaction of the first order. Atkins and Werner (*J. Chem. Soc.*, 1912, **99**, 1167) also found the reaction to be of the first order. The experimental work of Waddell was admittedly not accurate and the study of velocity by Atkins and Werner was confined to only one temperature. Their results, however, point to one fact that the products of reaction in both the direct and reverse reactions

have no influence on the velocity of the reaction. From the standpoint of the present investigation, what is of importance is the study of the temperature coefficient of the reaction rates. The work of Waddell and Atkins and Werner has therefore been revised with such improvements as were found necessary and possible and extended over a wide range of temperature.

In gaseous reactions to prove whether a reaction proceeds homogeneously or whether surface effects come into play, the reactions are caused to take place over inert surfaces and surface area per unit mass of reacting substance altered. In liquid systems this test can be applied only to a small degree. The reactions described in this paper were tested in this way by introducing into the reaction vessels strips of platinum and glass wool prepared of Jena glass.

EXPERIMENTAL.

The ammonium thiocyanate and thiourea used in this work were each twice recrystallised from alcohol. During the course of the work it was found that the removal of the last traces of alcohol from the crystals was necessary to prevent the formation of some foul smelling products. These were formed perhaps by side reactions in small quantities which, however, did not affect the velocity of reaction. The last traces of alcohol were removed by heating the crystallised substances at 100° for a long time and then desiccating in vacuum for some days before use. Thiocarbamide purified as above was found to melt at 179° and never below that. This is in accordance with the prediction of Findlay (*J. Chem. Soc.*, 1904, **85**, 402).

Two series of velocity measurements were made. In the first series almost equal quantities of ammonium thiocyanate and thiourea were introduced into a number of Jena glass bulbs which were then evacuated and sealed. Care was taken to see in all cases that traces of moisture, the substances might have absorbed during the filling of the bulbs, were completely removed by desiccation before sealing. About a dozen bulbs containing one of the substances at a time were put into a copper wire cage and immersed in an oil-thermostat of large capacity maintained at any desired temperature. The oil in the thermostat was kept well stir ed and

the temperature kept very constant. The bulbs were taken out at intervals, suddenly chilled by dropping them into cold water; they were then thoroughly cleaned outside, broken and the contents analysed.

In the second series of experiments long Jena glass tubes ($1\frac{1}{2}''$ diameter and $12''$ long) sealed at one end and provided at the top with a side tube which could be connected to a phosphorous pentoxide bulb were used. About 20 grams of either ammonium thiocyanate or thiourea were put into a tube of this type, closed at the top with a rubber cork and kept immersed almost up to the neck in the thermostat. The object of connecting the side tube at the top with a P_2O_5 bulb was to keep the air in the tube as dry as possible during the experiment. Small quantities of the molten liquid were withdrawn in Jena glass pipettes at intervals, suddenly chilled and then analysed.

The velocity measurements made in these two series of experiments gave absolutely identical results.

When the experiments had to be carried on below the melting points of the substances, the tubes were first of all maintained for a short time a little above the melting points of the substances when they melted and a certain amount of transformation took place. This lowered the melting point and then the tubes were transferred to the thermostat.

The effect of surfaces (as stated above) was tested by introducing platinum strips and Jena glass wool into the tubes used in the second series of experiments. Unfortunately it has not been possible to study the effect of solvents on the velocity as it has not been possible to get a convenient solvent which dissolves both the substances and is not volatile at temperatures when the reaction begins to proceed at measureable rates.

Method of Analysis.—The estimation of thiourea and ammonium thiocyanate in the presence of each other is a matter of considerable difficulty. After many trials the following procedure which gave excellent results was finally adopted. Thiourea was estimated in the mixture iodimetrically as recommended by Reynolds and Werner (*J. Chem. Soc.*, 1903, **83**, 1) and modified by Werner (*J. Chem. Soc.*, 1912, **99**, 2166). The solution just before titration was diluted such that the amount of thiourea present in 250 c. c. never exceeded 0·02 gm. Titration of a mixture of ammonium

thiocyanate and thiourea against mercuric nitrate solution in presence of dilute nitric acid using ferric nitrate as indicator gives a reading corresponding to thiocyanate plus thiourea in the mixture (Williams Lunge's *Technical Methods of Chemical Analysis*, p. 656). This method was first tested for mixtures of known composition, and finally adopted when it was found to give very reliable results. In all cases both thiourea and thiourea plus thiocyanate were estimated and the percentage composition calculated.

Equilibrium between Thiourea and Ammonium Thiocyanate.

For the calculation of the velocity constants it is necessary to know the equilibrium concentrations of the constituents in the reaction mixture. Burrows (*J. Amer. Chem. Soc.*, 1924, **46**, 1623) has studied the equilibrium of this system at different temperatures. It was thought desirable, however, to redetermine the equilibrium constant at the different temperatures at which velocity measurements were made.

The equilibrium was, at each temperature, approached from both sides. Table I gives the composition of the equilibrium mixtures, the equilibrium constants $k\dfrac{\text{conc. NH}_4\text{CNS}}{\text{conc. CS(NH}_2)_2}$, and the heats of reaction at different temperatures, as calculated from variation of equilibrium constants with temperature.

TABLE I.

Temp.	% Thiourea	k	Q(heat of reaction)
140°C	28·10	2·559	... 3271 calories
150°	26·24	2·811	
160°	24·56	3·071	... 3235 ,,
170°	23·09	3·300	... 3117 ,,
180°	21·76	3·595	... 3074 ,,
			Mean 3174 ,,

Rate of Reaction.

In a reversible reaction of the first order

$$A \underset{\longrightarrow}{\longleftarrow} B$$
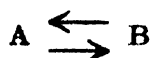
if we start with a gram molecules of A,

$$\frac{dx}{dt} = k_1(a-x) - k_2 x \dots\dots\dots\dots\dots(1)$$

where k_1 and k_2 are the velocities of the opposing reactions. If ϵ be the equilibrium value of x, then $k_1(a-\epsilon) = k_2\epsilon$ so that (1) may be written as

$$\frac{dx}{dt} = k_1(a-x) - k_2 \frac{(a-\epsilon)}{\epsilon} x$$

$$= k_1 + k_2(\epsilon - x)$$

If we were to start with a gram molecules of B instead of A, it can be shown that

$$\frac{dx}{dt} = k_1 + k_2(a - \epsilon - x)$$

so that for both the direct and reverse reactions we would get the same integration constant, *i.e.*, we get the same velocity constant from whatever direction we proceed. This, as pointed out by Waddell, forms a test for a reversible reaction of the first order. This condition is fulfilled in the reaction studied, as shown in Tables II, II(*a*), III and III(*a*) which contain the results obtained at 140° and 150°.
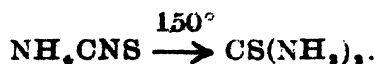
TABLE II.

$$NH_4CNS \xrightarrow{140°} CS(NH_2)_2.$$
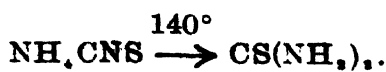
Time in min.	% Thiourea.	$e-x$	$k_1 + k_2$
0	6·92	21·18	——
30	8·94	19·16	0·003342
60	10·72	17·38	0·003291
90	12·29	15·81	0·003243
120	13·97	14·13	0·003369
180	16·82	11·28	0·003496
240	19·19	8·91	0·003601
360	23·05	5·05	0·003381
∞	28·10	0·00	0·003389 Mean

TABLE II(a).

$$CS(NH_2)_2 \xrightarrow{140°} NH_4CNS.$$
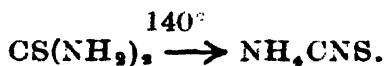
Time in min.	% Thiourea.		$k_1 + k_2$
0	62·10	34·0	——
30	58·79	30·69	0·003411
60	55·80	27·70	0·003411
90	52·82	24·72	0·003587
120	50·70	22·60	0·003399
150	48·50	20·45	0·003227
180	46·50	18·40	0·003406
∞	28·10		Mean 0·003365

TABLE III.

$$\text{NH}_4\text{CNS} \xrightarrow{150°} \text{CS(NH}_2)_2.$$

Time in min.	% Thiourea.	$a-x$	$k_1 + k_2$
0	4·169	22·07	......
15	7·126	19·11	0·009598
30	9·589	16·65	0·009384
45	11·347	14·89	0·008740
60	13·767	12·47	0·009506
75	16·382	9·86	0·010718
90	17·174	9·07	0·009869
∞	26·24		Mean 0·009636

TABLE III(a).

$$\text{CS(NH}_2)_2 \xrightarrow{150°} \text{NH}_4\text{CNS}.$$
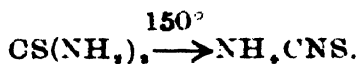
Time in min.	% Thiourea.	$a-c-x$	$k_1 + k_2$
0	52·95	26·71	—
15	49·34	23·10	0·009674
30	46·26	20·02	0·009605
45	43·42	17·18	0·009757
60	41·00	14·76	0·009874
75	39·25	39·01	0·009582
∞	26·24		Mean 0·009698

The difference between the two sets of values is within experimental error. k_1 represents the velocity constant for the direct

reaction $NH_4CNS \longrightarrow CS(NH_2)_2$, and k_2 the velocity constant for the reverse reaction. From the equilibrium constants at different temperatures, k_1 and k_2 could be computed. Table IV contains the summary of data thus obtained between 140° and 180°.

TABLE IV.

Temp.	$k_1 \times 10^4$	$k_2 \times 10^4$
140°C	9·999	25·58
150°	25·27	70·93
160°	60·90	187·02
160°(a)	62·10	190·71
160°(b)	61·20	187·94
170°	140·07	476·43
180°	305·42	1097·98

160°(a) and 160°(b) represent the results obtained with platinum and glass wool surfaces respectively; it will be seen that they are very much the same as without these surfaces.

. In Table V are given the temperature coefficients for k_1 and k_2 and the energies of activation of the two molecules at different temperatures. E_k refers to the heat of activation in calories.

TABLE V.

Temp.	Temp. coeff. (k_1)	E_{k_1}	Temp. coeff. (k_2)	E_{k_2}
140°C				
150°	2·53	32393 calories	2·77	35568 calories
160°	2·41	32185 ,,	2·63	35386 ,,
170°	2·30	31915 ,,	2·54	35717 ,,
180°	2·18	31248 ,,	2·:0	33393 ,,
		Mean 31935 ,,		Mean 35016 ,,

It will be noticed that the heat of reaction as calculated from equilibrium measurements (3174 cals.) is almost exactly equal to

the difference between the energies of activation of the two mole-
cules (which is equal to 3081 cals.) as is to be expected theoreti-
cally.

Discussion of Results.

The equation developed by Dushman (*J. Amer. Chem. Soc.*, 1921,
43, 397) and Rideal (*Phil. Mag.*, 1920, **40**, 461) for the velocity
of a unimolecular reaction has the form

$$k = \frac{E}{Nh} \; e^{-\frac{E}{RT}}$$

where $E = Nhv$ represents the critical increment in energy or the
energy of activation of the molecule. Velocity coefficients calculat-
ed with the help of this equation in the case of nitrogen pentoxide
decomposition both in the gaseous state and in solution agree pretty
well with the experimentally determined values. For purposes of
calculation this equation may be written in the form

$$\log k = 10{\cdot}0208 + \log E - \frac{E}{4{\cdot}571 \; T}.$$

In Table VI the calculated values for k_1 and k_2 are compared with
the experimentally determined values (the observed values given
in Table IV are here given, calculated for seconds).

TABLE VI.

Temp.	$k_1 \times 10^5$(obs.)	$k_1 \times 10_5$(cal.)	$k_2 \times 10^5$(obs.)	$k_2 \times 10^5$(cal.)
140°C	1·667	399	4·263	10·58
150°	4·212	1019	11·826	28·48
160°	10·150	2441	31·17	74·90
170°	23·345	5680	79·40	188·10
180°	50·903	12790	182·99	451·30

It is evident from the table that while the calculated values for k_1
are more than 200 times the observed values, the calculated values
for k are only 2·5 times the observed values. It may be pointed out

that a difference of about 500 calories in the energy of activiation as measured by the temperature coefficient is sufficient to cause such differences between the calculated and observed values as has been found in the case of k_2. It may therefore be said that in the case of the reverse reaction, *viz.*, $CS(NH_2)_2 \longrightarrow NH_4CNS$, Dushman's equation predicts the velocity of reaction pretty accurately. One cannot of course expect the Dushman—Rideal equation to hold both for the direct and reverse reactions in a case like the present one, where at the same temperatures the two reactions have almost the same temperature coefficients and the equilibrium constant remains almost the same.

The assumption in the Dushman—Rideal equation is the same as that in Lewis and Perrin's radiation hypothesis that $E = Nh\nu$, which means that a molecule to reach the active state absorbs one quantum of radiation of frequency ν. Calculations made on this basis predict absorption bands for molten ammonium thiocyanate and thiourea at $0·891 \mu$ and $0·812 \mu$ respectively. Unfortunately this could not be experimentally verified owing to the difficulty in dealing with these molten substances in infra-red spectroscopy.

The values of $\log k$ plotted against the reciprocals of absolute temperatures give for both the direct and reverse reactions very good straight lines. This is in accordance with the demands of the Arrhenius equation,

$$\log_{10} k = \frac{E}{2·3\ RT} + B.$$

In Table VII are given the values of B, calculated for each temperature for k_1 and k_2.

TABLE VII.

Temp.	$B (k_1)$	$B (k_2)$
$140°C$	12·14	14·17
$150°$	12·14	14·10
$160°$	12·14	14·10
$170°$	12·14	14·12
$180°$	12·14	14·09
Mean	12·14	Mean 14·10

$$\frac{Ek_1}{B} = 2630 \qquad\qquad \frac{Ek_2}{B} = 2483$$

These constants as well as $\frac{E}{B}$ are almost the same as for many other reactions (*cf.* Watson, *loc. cit.*).

According to Christiansen and Kramers (*Zeit. physikal. Chem.*, 1923, **104**, 451) this constant $B = \log_{10} A$ where $1/A$ represents what they call the 'active life' of the molecule. On this basis the active lives of NH_4CNS and $CS(NH_2)_2$ molecules are 7.24×10^{-12} and 8×10^{-14} seconds respectively. Whereas Christiansen and Kramers find that in most cases this is of the order of 10^{-14} seconds.

Summary and Conclusion.

The kinetics of the intramolecular transformation, $NH_4CNS \underset{\longleftarrow}{\overset{\longrightarrow}{}}$ $CS(NH_2)_2$ has been studied over the range $140-180°C$. It has been found that the velocity of reaction in either direction is not affected by the presence of air, or by platinum and glass surfaces. Even the presence of slight traces of alcohol and moisture in the substances, although they produce small quantities of foul smelling substances, have no influence on the velocity of reaction. So far as the results of the present investigations go, the reaction appears to proceed in a perfectly reversible unimolecular manner.

Equilibrium between NH_4CNS and $SC(NH_2)_2$ has been studied over the range $140-180°C$. It has been found that the heat of reaction as calculated from equilibrium data is exactly equal to the difference between the heats of activiation of the two molecules. This is in accordance with theory.

The Dushman—Rideal equation gives values in good agreement with observed values for the velocity constant of the reaction $CS(NH_2)_2 \longrightarrow NH_4CNS$ but not for the reverse reaction.

The constant B for the reaction has been calculated for both the reactions. These values are in good agreement with the values known for other reactions. From the standpoint of Christiansen

and Kramer's views, the active lives of the two molecules, NH_4CNS and $CS(NH_2)_2$ have been calculated and found to be 7.24×10^{-13} and 8×10^{-14} seconds respectively.

I wish to express my gratitude to Prof. J. C. Ghosh for his kind help, advice and encouragement during the progress of this work.

The Action of Light on Concentrated Aqueous Solution of Ammonium Thiocyanate.

By

S. S. Bhatnagar, H. B. Dunnicliff and Mohammad Ali.

Marshall Homes has recently investigated (*J. Chem. Soc.*, 1926, **129**, 1690) the cause of the red colouration which is developed when a concentrated aqueous solution of ammonium thiocyanate is exposed to sun-light and which slowly disappears on keeping the coloured solution in the dark. This phenomenon was originally described by Liesegang (Edor's *Jahrb. Photographic*, 1894, 49). On the strength of a rather small amount of experimental work, Holmes (*loc. cit.*) put forward the view that ammonium thiocyanate is decomposed into NH_4CN and sulphur according to the equation,

$$NH_4CNS = NH_4CN + S$$

and that the insoluble sulphur thus obtained forms larger aggregates of submicroscopic sizes which are responsible for the pink colour. These sub-microns slowly unite to form bigger particles and thus give rise to the small amount of precipitate which is obtained after long exposure.

The account of Marshall Holmes' researches reached the hands of the authors when they were already engaged on photochemical studies of a similar nature and it was considered desirable to study the phenomenon more fully as the equation of the reaction as given by Holmes did not seem to indicate the exact state of affairs. Since the colour of the solution completely disappears in the dark and can be produced again and again in the light, the problem appeared to be analogous to the reversible transformation of anthracene into dianthracene. the only completely reversible reaction fully described in literature and it thus presented another interesting aspect of study.

EXPERIMENTAL.

Since there is always the possibility that the iron in the glass vessels may be responsible for the colour so produced, the following critical experiments were tried to get decisive information on this point :—

(1) Instead of glass, quartz vessels were employed.

(2) To solutions of ammonium thiocyanate of varying concentrations (7·95N, 7·16N, 6·44N, 5·8N, 5·22N, 4·7N) very dilute ferric perchloride solutions acidified with HCl were added in amounts which just failed to produce the pink colour. The vessels were then exposed to sun-light. A control experiment with ammonium thiocyanate alone was also started at the same time. It was noticed that the colouration could be produced in quartz vessels quite as easily as in a glass vessel and the solutions described under (2) did not develop more colour than the control solutions nor was the action any quicker and hence the possibility that the reaction between the iron salt and the ammonium thiocyanate to produce the ferric thiocyanate may be catalysed was ruled out. The reaction appeared to be independent of the iron ions and quite distinct from the well-known action of ferric salts with ammonium thiocyanate.

Effects of Varying the Concentration of Ammonium Thiocyanate.

Solutions of varying concentrations were placed in the sun. The concentrations tried were, 9N, 8·1N, 7·29N, 6·56N, 5·9N, 5·31N and 4·78N. The colour was deepest in the strongest solution.

After about 5 hours' exposure a precipitate began to appear in 5·31N. When this precipitate begins to form, the colour gets visibly paler, a tinge of yellow mixing with the red colour of the solution. The precipitate appeared next in 5·9N and 4·78N and then in order of strength, being last to appear in the strongest solution.

The precipitate was most copious in 5·31N solution and least in the strongest solution. The order of the amount of precipitate was approximately 5·31N > 5·9N > 4·78N > 5·56N > 7·29N > 8·1N > 9N. It was found that solutions below 3·5N did not give any colouration.

But this depends on the kind of light.   On exposure to the December sun in the evening, even a solution of 4·5N did not get visibly coloured even after an exposure of half an hour.

Effect of the Intensity and Wave-length of Light on the Reaction.

In sunlight the pink colouration is developed in one minute, although in a very concentrated solution a faint pink can be discovered even after an exposure of ten seconds to the October sun. The precipitate takes from five to six hours to appear.   The quartz mercury vapour lamp and the light of iron arc produced a distinct pink in about 2 minutes.   The carbon arc, on the other hand, has a very feeble effect, even two hours' exposure to it being hardly equal to two minutes' exposure to the sun.

The colour goes on deepening with the length of exposure. Thus four days' exposure to the sun produced a deep red colouration. In order to find out which particular wave-lengths were most effective, a card-board box with seven compartments was made. Each compartment had for it a window cut out from the Wratten monochromatic light filters. Solutions of the same stength (8N) were placed behind each filter, and the box was closed so that light from no place except through the light-filter could fall on the various solutions.   The box was then lit up in sunlight for 6 hours. Violet light was found to be most effective.   Blue light produced a very faint colour, no other compartment showed the slightest effect. The same results were obtained when the exposure had been extended to three days. From the experiments on the iron and carbon arcs, it is clear that ultra-violet light is most effective, and that the effective region extends from blue to the ultra-violet.

Effect of Storage.—A solution (8N) which had been kept in the dark for 2 weeks gave a pink colour immediately on exposure to the sun, there being no difference from a freshly prepared solution of the same strength. Another solution of strength 9N which had been kept in the dark for more than a month also showed no difference in its behaviour from a freshly prepared one. This is opposed to the observation of Holmes who found that a solution which has been stored for sometime did not get coloured on exposure.

Effect of Moisture.—The dry crystals did not undergo any change on insolation. When placed in open air, however, they

absorbed moisture, being hygroscopic. The concentrated solution thus formed at the surface became pink on exposure to the sun.

Action of Solvents.—Carbon disulphide and benzene when shaken up with the coloured solution of NH_4CNS dissolved it to a certain extent, without getting coloured themselves. Ether was coloured pink and retained this colour in the dark.

Effects of Heating.—On heating a coloured solution of NH_4CNS, the colour was discharged, and ammonia was given off. The loss of colour was synchronous with the active evolution of ammonia. On exposing such a solution again, it developed a colour, which disappeared on heating. The effect could be repeated any number of times. An uncoloured solution of NH_4CNS also gave off ammonia on heating.

Acidity of Solution.—The unexposed as well as the exposed and coloured solutions were found to be acidic. The salt is hydrolysed in solution producing HCNS which is a strong acid.

Action of Various Substances.—(i) On dilution beyond $3·5N$, the colour disappeared.

(ii) The addition of alkalis, *e.g.*, KOH, NH_4OH in such amount as to make the NH_4CNS solution alkaline, discharged the colour. Such a solution on exposure to the sun developed no colour. KCN, as Holmes found, also produced the same effect, but this is due to the hydrolysis of KCN in solution and the production of KOH.

(iii) On the addition of acids the colour developed more rapidly. On the addition of dilute H_2SO_4 to a freshly prepared solution, a pink colour appeared without any exposure to light. After a time, reddish yellow crystals were precipitated and the solution was left pale yellow. This crystalline precipitate was quite different in appearance from the amorphous precipitate produced by sunlight, a qualitative analysis of which showed the presence of nitrogen, carbon and sulphur. This is probably perthiocyanic acid $C_2N_2H_2S_3$ which, as is well-known, is produced by action of acids on thiocyanates:
$$3HCNS = C_2N_2H_2S_3 + HCN \quad (\text{Völckel, } Annalen, 1842, 43, 74 ;$$
Richter's *Organic Chemistry*).

This action of acids is not characteristic of NH_4CNS only ; KCNS also behaves in the same manner.

(iv) The addition of a drop of freshly prepared solution of H_2S discharged the colour of 10 c.c. of a coloured solution of NH_4CNS.

The solution did not regain its colour on exposure to the sun, unless H_2S was boiled off. The action may be represented as follows.

$$HCNS + H_2S = CS_2 + NH_3 \quad \text{(Bernthsen's } Organic\ Chemistry).$$
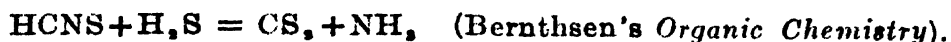
Effects of Air.—Holmes' experiments on exposing a solution of NH_4CNS in an evacuated vessel were repeated and confirmed. Besides that a tube with both the ends closed and having two side tubes provided with stop cocks was completely filled with a 50 per cent. solution of NH_4CNS. On exposure to light, the usual pink colour appeared, but after about an hour the colour began to be discharged until after about two hours, the solution was colourless. A very small amount of precipitate could be seen at the bottom. The experiment was repeated with a boiled out solution, and only a very faint pink colour was developed.

These experiments showed that oxygen was used up in the change, for in the first experiment, the change went on taking place so long as there was any oxygen left.

These conclusions were confirmed by exposing NH_4CNS solution under the atmospheres of gases like H_2 and CO_2 and it was found that no colour change took place.

These experiments rendered it probable that the reaction was due to oxidation. Effect of oxidising agents was. therefore, tried.

(i) *Hydrogen Peroxide.*—The addition of 1 drop of hydrogen peroxide solution to 10 c.c. of 8N solution of NH_4CNS produced a pink colour of exactly the same kind as that produced by sunlight. It behaved in the same manner with respect to dilution, alkalis, H_2S and the action of solvents. On allowing a solution coloured by hydrogen peroxide to stand, a yellow amorphous precipitate of the same description as the one produced by sunlight was obtained.

Other oxidising agents also produced the same colouration. The action of H_2O_2 gave a clue to the probable composition of the precipitate produced by sunlight. It is well known that H_2O_2 acting on alkali and ammonium thiocyanates produces pseudocyanogen sulphide $(CNS)x$; therefore the precipitate produced by sunlight was also likely to be $(CNS)_x$. This conclusion is rendered more probable in the light of Ganassini's work (*Boll. Chim. farm.*, 1919, **58**, 457). He observed that under the influence of light certain concentrations of potassium thiocyanate were oxidised by air to give pseudocyanogen sulphide according to the equation,

$$12KCNS + 12O_2 + 6H_2O = 6K_2SO_4 + 3HCN + 3CO_2 + 3NH_3 + 2(CNS)_3$$
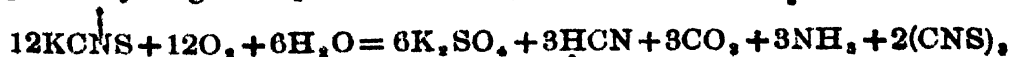
Experiments were tried to find out whether the same gases were given off in the oxidation of NH_4CNS. By bubbling pure air through cold solutions of NH_4CNS (which were exposed to the sun) and then through various reagents, negative results were found for NH_3 and HCN. But by another arrangement, in which a small amount of the reagent in a capillary tube could be brought in contact with the gases produced, many times, the following gases were detected :—

(i) NH_3 by Nessler's reagent ;

· (ii) SO_2 by $KMnO_4$ solution which was decoloured and precipitated hydrated manganese dioxide ;

(iii) HCN by the Schonbein-Pagenstacher test (*J. Chem. Ind.,* 1917, **35**, 196) which being extremely sensitive has the advantage of detecting HCN in presence of thiocyanates or HCNS.

(iv) CO_2 and H_2S were not detected,

Electrolysis of NH_4CNS Solution.—A further proof that the colour formation and the precipitate were due to the production of pseudocyanogen sulphide was afforded by the electrolysis of NH_4CNS solutions. Goppelsroeder (*J. Chem. Soc.,* Abs. 1885, **48**, 109) found pseudocyanogen sulphide on electrolysis of KCNS solution and in an appendix he acknowledges that A. Lidow found the same substance from NH_4CNS by electrolysis. He gave it the formula $C_3N_3HS_3$ but it is probable that the formula is $C_3N_3S_3$, as the results of analysis to be further described would show.

The experiment was repeated with concentrated solutions with a low current density in the hope that under such conditions the formation of $(CNS)_x$ would be preceded by a red colouration. The conclusion was found to be justified. At the anode a pink colour developed which behaved in the same manner with respect to reagents as the one produced by sunlight and at the cathode ammonia was given off. On passing the current for a longer time, the yellow precipitate of $(CNS)_x$ was obtained. The solution at the anode was acidic, at the cathode alkaline.

$$ NH_4CNS \;\rightleftharpoons\; NH_4{}^\circ + CNS' $$
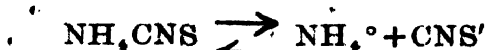
CNS' gets discharged and on polymerisation gives $(CNS)_x$ which is precipitated..

Spectroscopic Work.—But the most conclusive proof that the colour produced by sunlight is due to oxidation and is the same as that produced by oxidising the solution with H_2O_2 was afforded by a study of the absorption spectra of solutions of NH_4CNS coloured to the same extent under the action of sunlight and by H_2O_2.

Work with the Quartz Spectrograph of Adam Hilgers.—A 4t·8243 per cent. solution of NH_4CNS was divided into two portions. One was exposed to the sunlight for two days. Both the solutions were then spectrographed. The times of exposure for both the plates were the same ; they were developed in developers of the same strength and allowed to remain in the fixing bath for the same time. The length of the column of the liquid through which the light passed could be varied in a Baly's tube with quartz windows at the ends.

In dilute solution the absorption spectra in a column 93 mm. long were identical in the case of the coloured and the non-coloured solutions. The ultra-violet region is completely absorbed in both. No characteristic absorption bands were noticed.

The experiment was next repeated with a more concentrated solution (70·571 grams of NH_4CNS in 100 c.c. of solution) which had been exposed to the sun for four days and it was found that an absorption band appeared in the coloured solution, while in the uncoloured solution there was no such band.

Since the ultra-violet was totally absorbed, it was thought desirable to study the absorption spectra in the visible region by means of Adam Hilger Spectrometer of the constant deviation type. The visible region could be extended here and better resolution of lines in that region could be obtained.

The absorption spectra of the following solutions were studied :—

(*a*) A freshly prepared solution of NH_4CNS of concentration 70·571 per cent. (Plate No. 2).

(*b*) A solution of the same strength exposed to sunlight for 4 days (Plate No. 3).

(*c*) A solution of the same strength to which 0·1 c.c. of H_2O_2 was added (Plate No. 4).

(*d*) To a solution of 65 g. of NH_4CNS, 6 c.c. of H_2SO_4 diluted to twice their volume were added and the whole made up to 100 c.c. (Plate No. 5)

(e) To a solution of 65 g. of NH_4CNS, 6 c.c. of H_2SO_4 diluted to 12 c.c. were added and the whole made up to 100 c.c.

(f) A 10 per cent. solution of H_2SO_4 in water.

As may be seen from the plates, absorption bands appear only two cases :—

(1) The solution coloured by sunlight (Plate No. 3).

(2) The solution coloured by H_2O_2 (Plate No. 4) and these bands are exactly of the same type, thus proving that the action is the same in both the cases and that the same substance is produced.

With H_2SO_4 and NH_4CNS no characteristic bands appeared but the absorption spectra differed from the other solutions. That this is not due to the presence of H_2SO_4 is established by the fact that the absorption spectra of H_2SO_4 and water are quite different. This constitutes satisfactory evidence that the action of sunlight is to catalyse the oxidation of NH_4CNS solution by oxygen of the air and thus brings about the same reaction as is brought about by H_2O_2. It is also clear that although H_2SO_4 brings about a colour change similar, in outward appearance, to the colour change produced by sunlight ; the reaction is in reality quite different as indicated by the reaction equation cited in this paper.

Results of Chemical Analysis.—The final evidence in favour of the view put forward is afforded by the results of quantitative analysis.

Elements.	Percentage from the precipitate produced by sunlight (observed).	Percentage from the precipitate by addition of H_2O_2 (observed).	Percentage from (CNS). (calculated).
H	0·7	0·52	0·0
C	20·17	20·43	20·73
N	24·20	24·52	24·14
S	not determined	54·53	55·17

As the quantities of the precipitates obtained were very small, the results shown above may be considered to give a fair indication of the product being pseudocyanogen sulphide with the formula

The Carbon Arc.

53 mm. (length of the column of solution).

63 mm.

73 mm.

83 mm.

93 mm.

PLATE No. 1.

48·82·43% NH₄CNS.

The Carbon Arc.

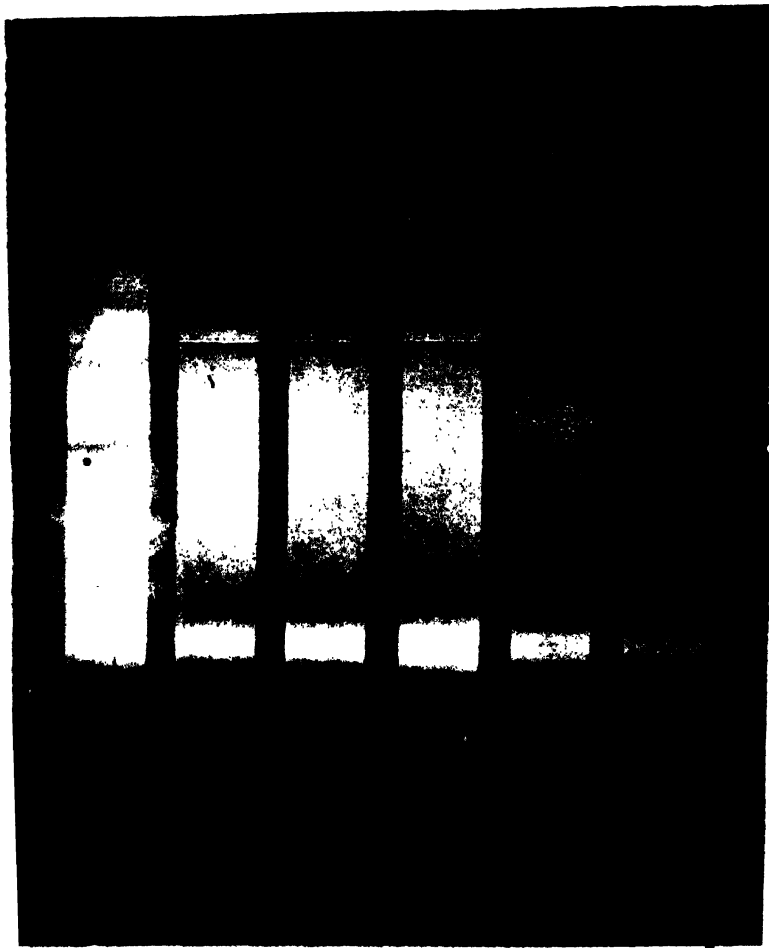53 mm. (length of the column of solution.[*]

63 mm.

73 mm.

83 mm.

93 mm.

PLATE No. 2.

70·571% NH$_4$CNS (uncoloured).

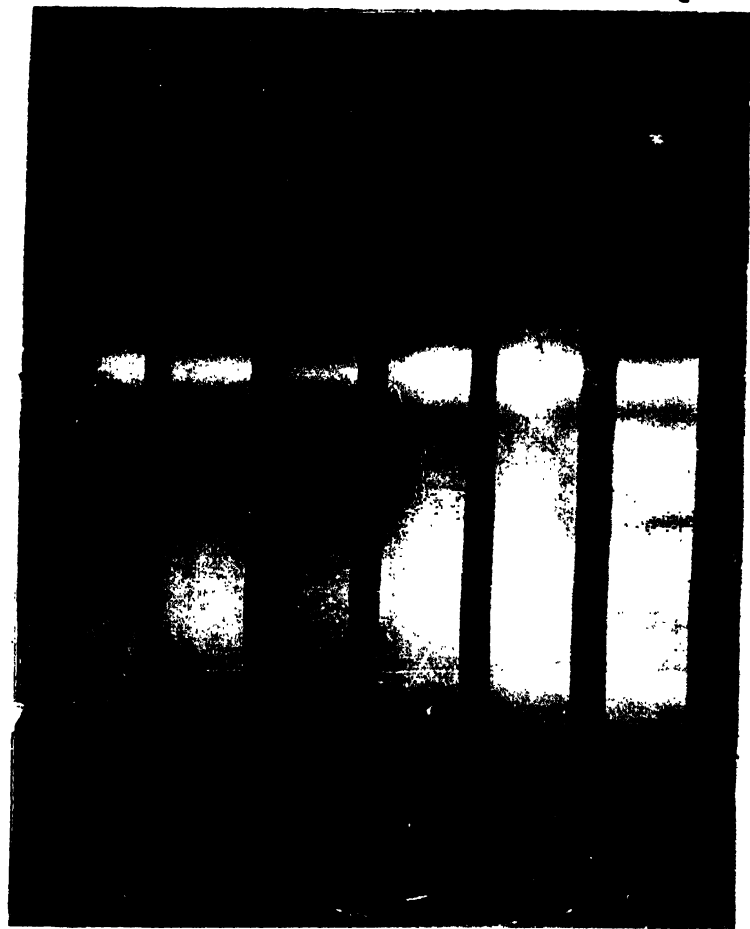The Carbon Arc.
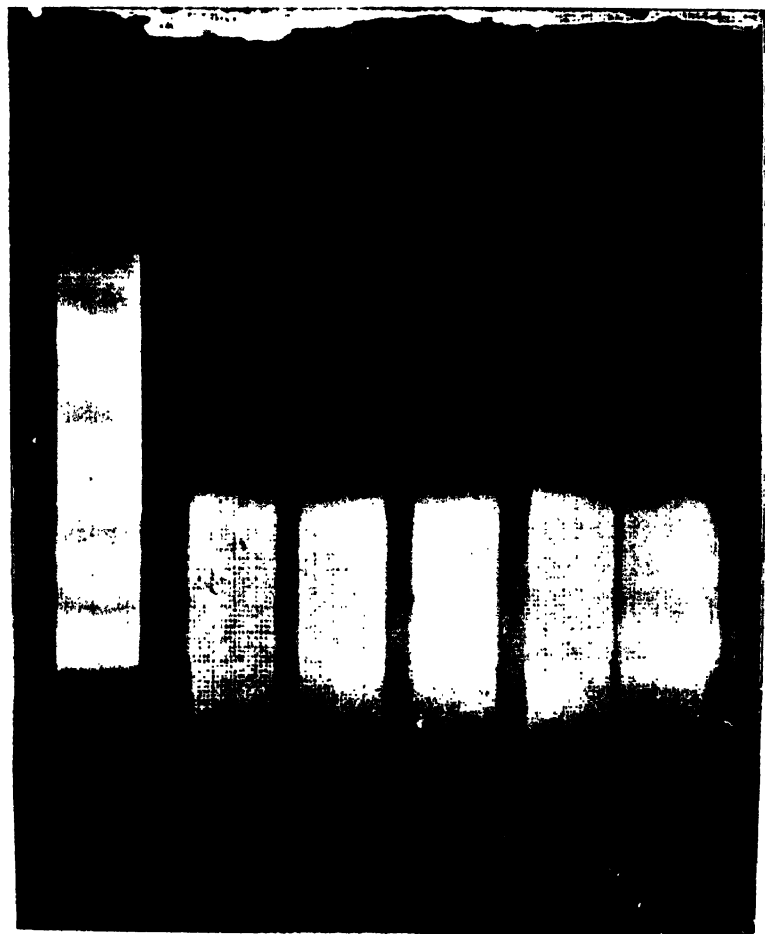
53 mm. (length of the column
of solution).

63 mm.

73 mm.

93 mm.

93 mm.

PLATE No. 3.

70·571% NH_4CNS coloured under the action of sunlight.

The Carbon Arc.

53 mm. (length of the column of solution).

63 mm.

73 mm.

83 mm.

93 mm.

PLATE No. 4.

70·571% NH$_4$CNS+0·1 c.c. of H$_2$O$_2$ (to 100 c.c. of solution).

The Carbon Arc.

53 mm. (length of the column
of solution).

63 mm.

73 mm.

83 mm.

93 mm.

PLATE No. 5.

.65% NH₄CNS+6 c.c. H₂SO₄ (to 100 c.c. of solution).

$(CNS)_x$. The hydrogen indicated in the table* probably came from moisture in the extremely small amounts of the precipitate available. * .

Summary of Results.

The production of colour and precipitate in concentrated solutions of ammonium thiocyanate by sunlight is due to oxidation by the oxygen of air catalysed under the action of sunlight. The principal evidences in favour of this view may be summed up thus :—

1. No colour appears when oxygen is absent, as on exhaustion or when an atmosphere of H_2 or CO_2 is maintained over the solution.

2. The pink colour and the precipitate produced are exactly of the same kind and behave in the same manner as the colour and precipitate produced by the addition of even a single drop of H_2O_2 to so much as 70 grams of NH_4CNS.

3. The absorption spectra of the coloured solution (by sunlight) and the one coloured by H_2O_2 are exactly of the same kind.

4. Analysis shows that the C and H content of both the precipitates is the same.

Possible Mechanism of the Reaction.—In view of the facts enumerated above it is probable that by oxidation of ammonium thiocyanate pseudocyanogen sulphide is produced, and since the change only takes place in presence of free HCNS, it is but reasonable to assume that NH_4CNS is hydrolysed by water to HCNS and NH_4OH ; and that HCNS is oxidised by oxygen to give CNS which is responsible for the colour.

This CNS further polymerises to give $(CNS)_x$, which is precipitated as pseudocyanogen sulphide.

$$NH_4CNS + H_2O \rightleftarrows NH_4OH + HCNS$$

$$2HCNS + O = H_2O + 2CNS$$

$$xCNS \longrightarrow (CNS)_x$$

The last two reactions are irreversible although at first the fact that in darkness the colour disappears, suggests that the action is reversible.   But the experiment above described of exposing a solution which contains dissolved air only to sunlight when the red coloured produced at first disappears giving a small precipitate shows that the action is irreversible.
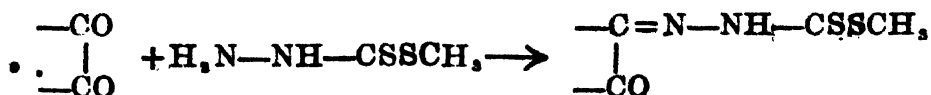
Formation of Heterocyclic Compounds. Part I. Action of Methyl-dithiocarbazinate upon *ortho*-Diketones and their Monoximes, and upon Chlorides and Esters of Dibasic Acids.

By Praphulla Chandra Guha and Sunil Chandra Guha.

The object of undertaking the present investigation was to make a comparative study of the behaviour of the o-diketones and their monoximes with other compounds possessing the grouping -NH·NH- e.g., hydrazines, semi- and thiosemi-carbazides, thiocarbohydrazide, on the one hand and with methyldithocarbazinate on the other. Curtius (*J. pr. Chem.*, 1881, **44**, 168, 188 ; *Ber.*, 1889, **22**, 2161) obtained different types of compounds by the action of hydrazine upon several o-diketones. Thiele and Stange (*Annalen*, 1894, **283**, 1) studied the action of thiosemicarbazide upon benzil and obtained a triazine compound. Schmidt and his collaborators (*Ber.*, 1911, **41**, 276, 3250) obtained a semicarbazone of phenanthraquinone and a triazine compound from its oxime. Guha and De (*J. Indian Chem. Soc.*, 1925, **2**, 228) obtained closed-ring thiocarbohydrazones from molecular proportions of thiocarbohydrazide and diketones like benzil, acenaphthaquinone, camphorquinone, and alloxan, whereas from two molecules of phenanthraquinone (as also β-naphthoquinone and isatin) and one molecule of thiocarbohydrazide they obtained di-phenanthraquinone-thiocarbohydrazone. Guha and De (*J. Indian Chem. Soc.*, 1926, **3**, 41) prepared heptatriazine compounds from molecular proportions of o-aminophenyihydrazine and a number of o-diketones.
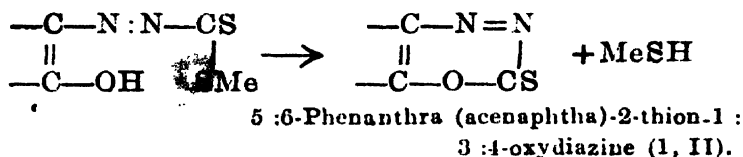
One molecule of methyldithiocarbazinate reacts with one ketonic group of phenanthraquinone and acenaphthaquinone to form the corresponding hydrazone methyl dithiocarboxylates as intermediate products, thus :
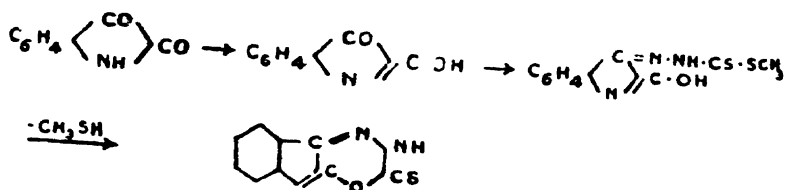
$$\begin{matrix} -CO \\ | \\ -CO \end{matrix} \quad +H_2N-NH-CSSCH_3 \longrightarrow \begin{matrix} -C=N-NH-CSSCH_3 \\ | \\ -CO \end{matrix}$$

which then assumes the azo structure by migration of one hydrogen atom,

$$\begin{matrix} -C=N-NH-CSSMe \\ | \\ -CO \end{matrix} \quad \longrightarrow \quad \begin{matrix} -C-N=N-CSSMe \\ || \\ -C-OH \end{matrix}$$

Similar cases of migration resulting in the change of hydrazones into azo compounds are well known (*cf.* Liebermann, *Ber.*, 1883, **16**, 2863 ; Zincke and Lawson, *Ber.*, 1887, **20**, 2903; Meldola, *Phil. Mag.*, 1888, **11**, 411; Guha and De, *loc. cit.*). The azo-compounds then lose a molecule of methyl mercaptan giving rise to oxydiazine compounds (I, II) thus :
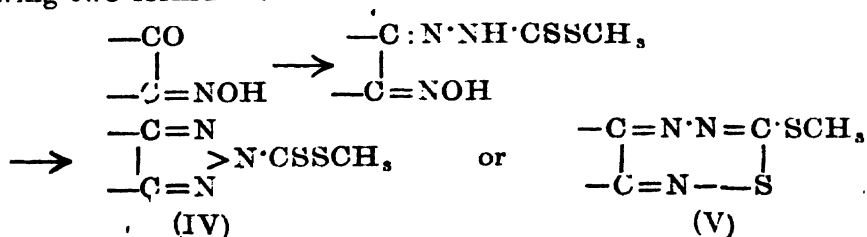
$$\begin{array}{ccc} -\text{C}-\text{N}:\text{N}-\text{CS} & & -\text{C}-\text{N}=\text{N} \\ \| & \downarrow & \| & | & +\text{MeSH} \\ -\text{C}-\text{OH} \quad \text{Me} & \rightarrow & -\text{C}-\text{O}-\text{CS} \end{array}$$

5 :6-Phenanthra (acenaphtha)-2-thion-1 :
3 :4-oxydiazine (1, II).

With isatin the reaction proceeds thus :—

$$\text{C}_6\text{H}_4\left\langle\begin{array}{c}\text{CO}\\\text{NH}\end{array}\right\rangle\text{CO} \rightarrow \text{C}_6\text{H}_4\left\langle\begin{array}{c}\text{CO}\\\text{N}\end{array}\right\rangle\text{C}\cdot\text{OH} \rightarrow \text{C}_6\text{H}_4\left\langle\begin{array}{c}\text{C}=\text{N}\cdot\text{NH}\cdot\text{CS}\cdot\text{SCH}_3\\\text{N}\end{array}\right\rangle\text{C}\cdot\text{OH}$$

$$\xrightarrow{-\text{CH}_3\text{SH}}$$

That this compound contains a thiol group is proved by the fact that it is soluble in alkali and readily gives insoluble lead and mercury mercaptides and monoacetyl and monobenzoyl derivatives.

Benzil reacts with methyl dithiocarbazinate with the liberation of hydrogen sulphide and methyl mercaptan. The resulting product possesses a sharp melting point but curious as it appears, it does not contain any nitrogen.

Two molecules of water are eliminated from one molecule of phenanthraquinone monoxime and one molecule of NH_2—NH—CSSMe with the formation of a compound possessing the empirical formula $\text{C}_{16}\text{H}_{11}\text{N}_3\text{S}_2$ which may be represented by either of the following two formulae.

$$\begin{array}{cc} -\text{CO} & -\text{C}:\text{N}\cdot\text{NH}\cdot\text{CSSCH}_3 \\ | & \rightarrow & | \\ -\text{C}=\text{NOH} & -\text{C}=\text{NOH} \end{array}$$

$$\rightarrow \quad \begin{array}{c} -\text{C}=\text{N} \\ | \quad\quad >\text{N}\cdot\text{CSSCH}_3 \\ -\text{C}=\text{N} \end{array} \quad \text{or} \quad \begin{array}{c} -\text{C}=\text{N}\cdot\text{N}=\text{C}\cdot\text{SCH}_3 \\ | \quad\quad\quad\quad | \\ -\text{C}=\text{N}--\text{S} \end{array}$$
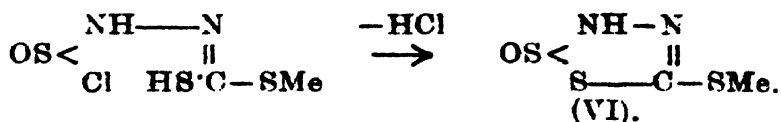
(IV)   (V)

The osotriazole-methyldithiocarboxylate (IV) on hydrolysis by alkali and on subsequent acidification should yield the free thio-acid and methyl mercaptan. But in actual practice, no such thing was observed. Hence, thioheptatriazine formula (V) is given preference to the osotriazole formula (IV).

Isatin monoxime does not react with the carbazinate showing that the monoxime does not possess any active ketonic group.
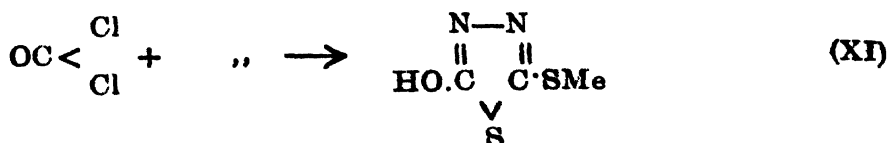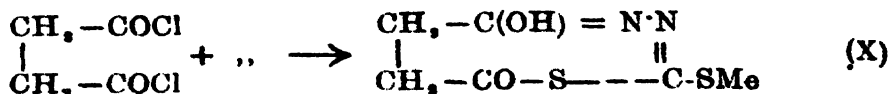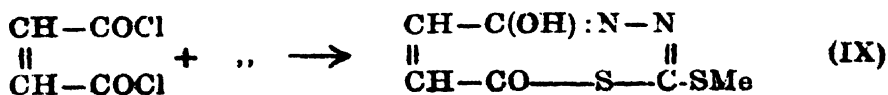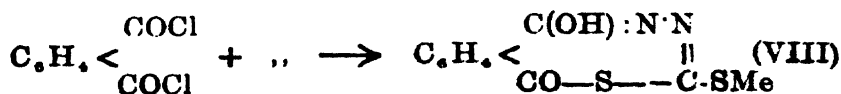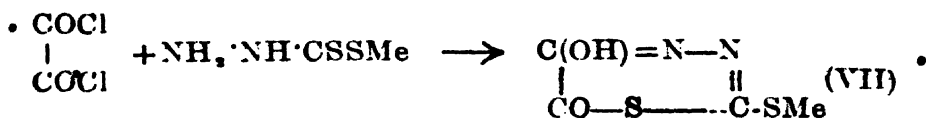
The action of six different acid chlorides (*viz.* thionyl, oxalyl, phthalyl, fumaryl, succinyl, carbonyl) upon the carbazinate has been studied. With thionyl chloride the reaction proceeds thus :

$$SOCl_2 + NH_2 \cdot NH \cdot CS \cdot SMe \longrightarrow OS\begin{matrix} NH \cdot NH \cdot CS \cdot SMe \\ Cl \end{matrix} + HCl$$

This intermediate product then loses another molecule of hydrochloric acid to yield methyldithiocarbazinate sulphite.[*]

$$OS\begin{matrix} NH \text{----} N \\ \| \\ Cl \quad HS \cdot C \text{---} SMe \end{matrix} \xrightarrow{-HCl} OS\begin{matrix} NH \text{---} N \\ \| \\ S \text{----} C \text{---} SMe. \end{matrix}$$
(VI).

With oxalyl, phthalyl, fumaryl, succinyl and carbonyl chlorides the reactions proceed in a similar fashion forming respectively 6-keto-5-hydroxy-2 methylthiol-1 : 3 : 4-thiodiazine (VII), 2-methylthiol-5-hydroxy-6 : 7-benzo-1-keto-1 : 3 : 4-octathiodiazine (VIII), 2-methylthiol-5-hydroxy-8-keto-1 : 3 : 4-octathiodiazine (IX), 2-methylthiol-5-hydroxy-6 : 7-dihydro-8-keto-1 : 3 : 4-octathiodiazine (X) and 2-hydroxy-5-methylthiol-1 : 3 : 4-thiodiazole (XI) thus :

$$\begin{matrix} COCl \\ | \\ COCl \end{matrix} + NH_2 \cdot NH \cdot CSSMe \longrightarrow \begin{matrix} C(OH) = N \text{---} N \\ | \qquad\qquad \| \\ CO \text{----} S \text{------} C \text{-} SMe \end{matrix} \quad (VII)$$

$$C_6H_4 \begin{matrix} COCl \\ COCl \end{matrix} + \text{,,} \longrightarrow C_6H_4 \begin{matrix} C(OH) : N \cdot N \\ \| \\ CO \text{---} S \text{--} C \text{-} SMe \end{matrix} \quad (VIII)$$

$$\begin{matrix} CH \text{---} COCl \\ \| \\ CH \text{---} COCl \end{matrix} + \text{,,} \longrightarrow \begin{matrix} CH \text{---} C(OH) : N \text{---} N \\ \| \qquad\qquad\qquad \| \\ CH \text{---} CO \text{----} S \text{----} C \text{-} SMe \end{matrix} \quad (IX)$$

$$\begin{matrix} CH_2 \text{---} COCl \\ | \\ CH_2 \text{---} COCl \end{matrix} + \text{,,} \longrightarrow \begin{matrix} CH_2 \text{---} C(OH) = N \cdot N \\ | \qquad\qquad\qquad \| \\ CH_2 \text{---} CO \text{-} S \text{------} C \text{-} SMe \end{matrix} \quad (X)$$

$$OC \begin{matrix} Cl \\ Cl \end{matrix} + \text{,,} \longrightarrow \begin{matrix} N \text{---} N \\ \| \quad \| \\ HO.C \quad C \cdot SMe \\ V \\ S \end{matrix} \quad (XI)$$

[*] *Cf.* similar reactions of 1-substituted thiosemicarbazides with phosgene (Freund, *Ber.*, 1891, **24**, 4178) and with thiophosgene (*Ber.*, 1890, **23**, 2943).

A corresponding 3-*N*-phenylthiodiazole compound of type (XI) was prepared by Busch from PhNH.NH.CSSMe by the action of phosgene (*J. pr. Chem.*, 1899, **60**, 34). The easy formation of a closed ring compound (IX) from fumaryl chloride in which the COCl groups occupy *trans*-positions with respect to each other can only be explained by assuming a transformation of the *trans* into the *cis* form under the conditions of the experiment.

EXPERIMENTAL.

Phenanthraquinone and Methyl dithiocarbazinate : Formation of 2-Thion-5 : 6-phenanthro-1 : 3 : 4-oxydiazine (I).

An alcoholic solution of phenanthraquinone (2·1 g.) and methyl-dithiocarbazinate (1·2 g.) was heated under reflux. The reaction began at once as was indicated by the evolution of mercaptanic smell. The solution turned red and a red crystalline precipitate began to separate out. This was filtered hot and recrystallised from pyridine as light red needles, m. p. 205°-206° (yield 2 g.). It is insoluble in dilute alkalis and dissolves in concentrated sulphuric acid producing a dark green colouration. (Found : N, 10·10; S, 11·60. $C_{15}H_8ON_2S$ requires N, 10·61; S, 12·12 per cent.).

The above experiment when repeated using 2 molecules of methyldithiocarbazinate with one molecule of phenanthraquinone yielded the same compound.

2-Thion-5 : 6-acenaphtho-1 : 3 : 4-oxydiazine (II).

A mixture of acenapthaquinone (1·8 g.) and methyldithiocarba-zinate (1·2 g.) was heated in acetic acid solution under reflux for four to five hours. A brownish red solid mass began to separate with the evolution of mercaptanic smell. The separated solid was filtered from the mother-liquor while hot, washed with acetic acid and puri-fied by crystallization from dilute pyridine when needle-shaped crystals were obtained, m. p. 208°-209° with decomposition. It is insoluble in alkali and produces a dark-brown colouration with strong sulphuric acid. Yield 2 gms. (Found : N, 12·07. $C_{13}H_6ON_2S$ requires N, 11·76 per cent.).

2-Thiol-5 : 6-isato-1 : 3 : 4-oxydiazine (III).

By heating isatin (1·5 g.) and methyldithiocarbazinate (1·3 g.) in acetic acid solution under reflux, a deep yellow precipitate was

obtained which was crystallized from acetone, m. p. 227° with decomposition. It is soluble in dilute sodium hydroxide solution from which it can be precipitated by hydrochloric acid and gives a red colouration with concentrated sulphuric acid. (Found: N, 20·30. $C_9H_5ON_3S$ requires N, 20·69 per cent.).

The *benzoyl derivative* prepared by the Schotten Bauman process was crystallised from a very small quantity of acetone, m. p. 228°-229°. Mixed melting point with the original isatin condensation product is 208-209°. (Found: N, 13·11. $C_{16}H_9O_2N_3S$ requires N, 13·68 per cent.).

The *acetyl derivative* was obtained by heating the isatin condensation product with acetic anhydride for about twenty minutes under reflux and then pouring into water. It was purified by repeated crystallisation from water, m. p. 161°-162°. (Found: N, 16·75. $C_{11}H_7O_2N_3S$ requires N, 17·14 per cent.).

Benzil and Methyl-dithiocarbazinate.

A mixture of benzil (2 g.) and methyl dithiocarbazinate (1·2 g.) was heated under reflux in acetic acid solution for 12 hours, during the first four hours' heating there being no appreciable change. The excess of acetic acid was removed by distillation under reduced pressure, the solution was cooled and the small quantity of the yellow substance thus obtained was crystallised from acetone, m. p. 195°. It was found to contain only sulphur, carbon and hydrogen. It is insoluble in dilute caustic soda solution. (Found: S. 44·67 per cent). As the yield of the product was only 0·15 grams, a thorough study of its properties as also an analysis for carbon and hydrogen could not be made.

Phenanthraquinone monoxime and Methyldithiocarbazinate: Formation of 3:4-Phenanthra-7-thiomethyl-1:2:5:6-heptathiotriazine (V).

A mixture of phenanthraquinone monoxime (1 g.) and methyl-dithiocarbazinate (1 g.) was heated in alcoholic solution under reflux for about 8 hours. On cooling a brownish red precipitate came out which was crystallised from pyridine in needles, m. p. 209°-210° with decomposition. It is insoluble in dilute cold sodium hydroxide solution. (Found : N, 13·45. $C_{16}H_{11}N_3S_2$ requires N, 13·55 per cent.).

Methyl dithiocarbazinate and Isatin Monoxime.

By treating molecular proportions of isatin monoxime and methyl dithiocarbazinate in a similar manne. as in the foregoing experiment and also by heating the mixture at 100˙ in a sealed tube for about twelve hours, isatin monoxime was found to have been left unconverted.

Methyl dithiocarbazinate Sulphite.

Thionyl chloride (2 g.) in benzene solution was gradually added to a benzene solution of methyl dithiocarbazinate (2 g.) when a violent reaction ensued with the separation of a yellowish white solid substance. It was filtered, washed with benzene and crystallised from dilute acetone. The yield was almost quantitative. It shrinks at 100° and melts at 122˙-123°. It is soluble in cold sodium hydroxide solution. (Found : N, 17·15. $C_2H_4ON_2S_2$ requires N, 16·67 per cent.).

2-Methylthiol-5-hydroxy-6-keto-1 : 3 : 4-thiodiazine (VII).

The solid product obtained by mixing benzene solutions of oxalyl chloride and methyl dithiocarbazinate was found to be insoluble in all ordinary organic solvents. It was, however, purified by dissolving in dilute sodium hydroxide solution and fractionally precipitating with dilute hydrochloric acid. The process of fractional precipitation was repeated once again. It melts at 127˙ with decomposition. (Found : N, 16·33; S, 35·94. $C_4H_4O_2N_2S_2$ requires N, 15·91; S, 36·36 per cent.).

The acetyl derivative. prepared in the usual manner, was purified by crystallising twice from dilute alcohol, m. p. 174 -175 . (Found : N, 12·34. $C_6H_6O_3N_2S_2$ requires N, 12·84 per cent.).

2-Methylthiol-5-hydroxy-6 : 7-benzo-8-keto-1 : 3 : 4-octathiodiazine (VIII).

The solid product obtained by heating a benzene solution of phthalyl chloride (2 g.) and methyl dithiocarbazinate (1·2 g.) under reflux for 5-10 minutes, was crystallised from dilute alcohol in shining plates. The compound shrinks at 155˙ and melts at 161°-162°, and is soluble in cold sodium hydroxide solution. (Found : N, 10·76. $C_{10}H_8O_2S_2N_2$ requires N, 11·11 per cent.).

2-Methylthiol-5-hydroxy-8-keto-1 : 3 : 4-octathiodiazine (IX).

By proceeding as in the previous experiment, a solid product (2 g.) was obtained from fumaric chloride (1·5 g.) and methyl dithiocarbazinate (1·2 g.). The substance could not be crystallised from the common organic solvents; however a saturated solution of the substance in boiling aqueous acetone solution gave, on cooling, a white amorphous precipitate melting with decomposition at 171°. (Found : N, 13·64; S, 31·24. $C_6H_6O_2N_2S_2$ requires N, 13·86; S, 31·68 per cent.).

2-*Methylthiol-5-hydroxy-6 : 7-dihydro-8-keto-1 : 3 : 4-octathiodiazine* (X).

The sold product (1·5 g.) obtained from succinyl chloride (1·5 g.) and methyl dithiocarbazinate (1·2 g.) could not be crystallised from any organic solvent. An aqueous solution of this substance was boiled with animal charcoal for half an hour, filtered, the filtrate evaporated almost to dryness which on cooling gave a yellow crystalline substance. m. p. 137° with decomposition. It turns brownish-red on exposure to the air. (Found : N, 13·96; S, 30·94. $C_6H_8O_2N_2S_2$ requires N, 13·73; S, 31·37 per cent.).

2-*Hydroxy-5-methylthiol-1 : 3 : 4-thiodiazole* (XI).

A mixture of 4 gms. of 30 % solution of phosgene in toluene and 1·2 gms. of methyl dithiocarbazinate suspended in 5 c.c. of toluene was shaken for half an hour in a shaking machine and allowed to stand overnight. Next day, the solid product was washed repeatedly with toluene and was crystallised in needles form a small quantity of water, m.p. 96-97 after shrinking at 91° (yield quantitative). The compound is soluble in cold dilute sodium hydroxide solution. (Found : N, 19·39. $C_3H_4ON_2S_2$ requires N, 18·92 per cent.).

Action of Methyl dithiocarbazinate on Oxalic Ester : Formation of (VII).

Oxalic ester (1·5 g.) and methyl dithiocarbazinate (1·2 g.) in alcoholic solution were heated at 100° for 12-13 hours in a sealed tube. The solution, on evaporation on a water-bath, yielded a semi-solid mass which when pressed on a porous plate gave a yellowish white solid substance. It was identical with the condensation

product of oxalyl chloride and methyl dithiocarbazinate and was similarly purified. (Found : N, 16·32. $C_4H_4O_2N_2S_2$ requires N, 15·91 per cent.).

Condensation of carbonic ester with methyl dithiocarbazinate in alcoholic solution was tried by the method similar to that described in the previous operation, but no reaction was found to have taken place.

Our thanks are due to Sir P. C. Ray and Dr. J. C. Ghosh for the kind interest they have taken in this work.

Dyes derived from Itaconic Acid.

By Prasanta Ratan Dhar and Sikhibhushan Dutt.

Itaconic acid resembles succinic acid in some physical and chemical properties, e.g., in solubility and in formation of anhydride, acid chloride and imide. But from the point of view of molecular strain itaconic acid, which is methylene succinic acid, on account of its unsaturated linkage, contains a more strained system than succinic acid, and therefore it was expected that dyes derived from itaconic acid by condensation with various aromatic hydroxy and amino compounds would have more colour than the corresponding derivatives of succinic acid (cf. Dutt, J. Chem. Soc., 1926, **129**, 1171). It has been found in practice that the condensation products of itaconic acid, which have been thus obtained, have a deeper colour than the corresponding succineïns.

Itaconic acid condenses with aromatic hydroxy and amino compounds directly, but it has been found that the addition of a suitable condensing agent leads to a much better yield. Sulphuric acid and tin tetrachloride have been found to be the most suitable in this respect. The constitution of these compounds can be represented as follows, regarding the phenol- and resorcinol-itaconeïns as typical members : —
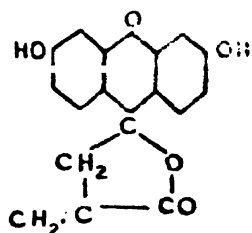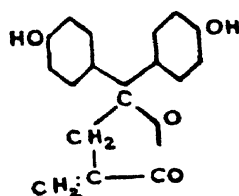
Resorcinol itaconeïn.   Phenol-itaconeïn.

The following aromatic hydroxy and amino compounds have been condensed with itaconic acid and the corresponding itaconeïns obtained :—phenol, resorcinol, catechol, phloroglucinol, pyrogallol and

m-diethylamido-phenol. The condensation product with resorcinol has been brominated and a hexa-bromo compound obtained. This bromo compound, which dissolves in dilute alkalis with a brilliant crimson colour, has been found by direct comparison to have a more intense colour, and stronger dying properties than ordinary eosin, which is tetrabromo-resorcinol-phthalein, and than tetra-bromo-resorcinol succinein. This greatly intensified colour development is probably due to the two extra bromine atoms.

The condensation product with catechol has been obtained in the form of a-hydrochloride, which, from its chemical properties, seems to be an oxonium derivative. The hydrochloride is easily decomposed by water into hydrochloric acid and catechol-itaconein, but its tin chloride double salt seems to be stable and dissolves in water with an intense magenta colour.

In general properties, colour and fluorescence, it has been found that the dyes derived from itaconic acid are similar to the corresponding substances obtained from succinic acid.

EXPERIMENTAL.

Phenol-itaconein.

A mixture of itaconic acid (5 g.) phenol (14·6 g.)and tin tetra-chloride (25 g.) was heated on the water-bath under reflux for 16 hours. The product was poured into water and the excess of phenol distilled off in steam. The residue was then extracted with dilute ammonia and the extract, after filtration, was treated with dilute hydrochloric acid. The greyish white precipitate of the crude phenol-itaconein thus obtained was purified by dissolving in dilute ammonia and precipitating with dilute hydrochloric acid a number of times until it was almost white in appearance; m. p. 210°.

The substance is very soluble in the ordinary organic solvents and also in alkalis in which it dissolves with a brilliant pink colour. (Found: C, 72·01 ; H, 5·7. $C_{17}H_{14}O_4$ requires C, 72·35; H, 4·9 per cent.).

Resorcinol-itaconein.

A mixture of itaconic acid (3·9 g.) and resorcinol (6·6 g.) was heated on the oil-bath at 130-140° for nearly 3 hours with the

addition of sulphuric acid (0·5 c.c.). The melt after cooling was dissolved in alcohol and treated with an alcoholic solution of lead acetate. The bright orange precipitate of the lead lake was filtered off, washed with alcohol and then decomposed with hydrogen sulphide in alcoholic suspension. The precipitated lead sulphide was removed and the alcoholic mother-liquor, on concentration to a small volume and cautious dilution with water, yielded the resorcinol-itaconeïn in the form of a bright yellow crystalline powder. By repetition of the above process a number of times the substance was obtained in a pure condition, m. p. 195° (decomp.).

The substance is very soluble in alcohol, acetone and acetic acid, but insoluble in ether, benzene, ligroin and water. It dissolves in alkalis with a yellow colour, and the solution on dilution shows a brilliant green fluorescence. The solution in organic solvents also shows similar fluorescence. (Found : C, 68·69 ; H, 3·99. $C_{17}H_{12}O_6$ requires C, 68·9 ; H, 4·00 per cent.).

Catechol-itaconeïn (hydrochloride).

$$\begin{matrix} C_3H_4 \\ CO - O \end{matrix} \Big\rangle C \Big\langle \begin{matrix} C_6H_3(OH) \\ C_6H_3(OH) \end{matrix} \Big\rangle O \Big\langle \begin{matrix} H \\ CL \end{matrix}$$
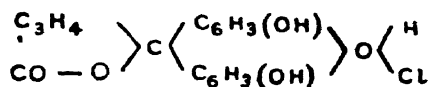
A mixture of itaconic acid (6 g.), catechol (10·15 g.) and tin tetrachloride (25 g.) was heated on the water-bath under reflux for 3 hours. The melt was then poured into water in which it dissolved completely forming a magnificent magenta coloured solution containing a tin chloride double salt. The solution was acidulated with dilute hydrochloric acid and treated with hydrogen sulphide until the tin was completely precipitated. The light pink coloured filtrate from the precipitated tin sulphide was concentrated to a small volume and kept in a desiccator containing quick lime and caustic potash for nearly a week when masses of colourless crystals appeared. These were filtered and dried in a vacuum desiccator ; m. p. 165° (decomp.).

The substance is extremely soluble in water and is highly hygroscopic. The colourless solution in water on treatment with dilute alkali develops a dirty pink colour which is discharged on the

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addition of acid. It contains one molecule of hydrogen chloride and its chemical properties indicate that it is an oxonium derivative. (Found : C, 61·5 ; H, 3·6 ; Cl, 10·8. $C_{17}H_{13}O_8Cl$ requires C, 61·44 ; H, 3·9 ; Cl, 10·5 per cent.).

Phloroglucinol-itaconein.

Phloroglucinol (9·7 g.) and itaconic acid (5 g.) were mixed and heated on an oil-bath at 130-140° for three hours with the addition of a few drops of sulphuric acid. The melt was dissolved in dilute sodium hydroxide solution and after filtration was treated with dilute hydrochloric acid. The precipitate was purified by solution in alkali and reprecipitation with dilute acid in the same manner a number of times until it was obtained in a crystalline condition; m. p. above 290° (decomp.).

It is a dark brown substance which is moderately soluble in organic solvents and very soluble in alkalis in which it dissolves with a blood-red colour. The solution is not fluorescent. (Found : C, 61·8 ; H, 3·8. $C_{17}H_{12}O_7$ requires C, 62·2 ; H, 3·6 per cent.).

Pyrogallol-itaconein.

A mixture of itaconic acid (6 g.), pyrogallol (11·6 g.) and tin tetrachloride (25 g.) was heated on the water-bath under reflux for six hours. The melt was poured into water when a mauve coloured precipitate was obtained. It was dissolved in hot concentrated hydrochloric acid, the solution diluted with water and then the tin completely precipitated from solution by hydrogen sulphide. The filtrate from the tin sulphide was evaporated to a small volume and kept in a desiccator containing quick lime and caustic potash for nearly a week at the end of which the colouring matter separated in masses of black crystals. These were filtered off, washed with water and then dried in a vacuum desiccator.

The substance is slightly soluble in organic solvents and insoluble in water. It is very soluble in concentrated acids and also in

alkalis in which it dissolves with a dirty pink colour; m. p. 253°
(decomp.). (Found : C, 62·3 ; H, 3·2 ; $C_1H_{12}O_7$ requires C, 62·9 ;
H, 3·6 per cent.).

m-Diethylamidophenol-itaconcïn.

A mixture of itaconic acid (6 g.) and *m*-diethylamidophenol
(15·2 g.) was heated on the oil-bath at 130-140° with a few drops
of sulphuric acid for five hours. The cold melt was extracted with
dilute hydrochloric acid and the filtered extract precipitated with
dilute sodium carbonate. The tarry precipitate was dissolved in
alcohol and the solution boiled with animal charcoal and filtered.
From the filtrate the alcohol was distilled off and the residue dis-
solved in dilute hydrochloric acid and reprecipitated with sodium
carbonate solution. The substance was thus obtained in dark
pink crystals which were collected and dried in a vacuum desic-
cator; m. p. 80° (decomp.).

The substance is very soluble in organic solvents and in dilute
acids with a bright pink colour and a deep brown fluorescence.
(Found : N, 6·5. $C_{28}H_{30}O_3N_2$ requires N, 6·8 per cent.).

Tetrabromo-resorcinol-itaconcïn-dibromide.

$$\begin{array}{c} C_3H_4Br_2 \\ | \\ CO \underline{\quad\quad} O \end{array} \rangle C \langle \begin{array}{c} C_6HBr_2(OH) \\ C_6HBr_2(OH) \end{array} \rangle O$$
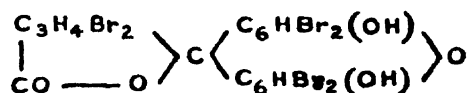
Resorcinol-itaconeïn (1 mol.) was brominated in glacial acetic
acid solution with excess of bromine (7 mol.) by heating on the
water-bath under reflux for an hour. The solution was then
poured into water and the blood-red precipitate of the eosin thus
obtained collected and washed with water, and dried in the steam
oven. The substance was thus obtained as fine crystalline powder,
m. p. 187° (decomp.).

The substance is moderately soluble in organic solvents and very
soluble in alkalis in which it dissolves with a brilliant violet red
colour. The solution is not fluorescent. (Found : Br, 62·0.
$C_{17}H_8O_6Br_6$ requires Br, 62·1 per cent.).

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Dyes Derived from Citraconic Acid.

By Prasanta Ratan Dhar and Sikhibhushan Dutt.

The object of the present investigation was to prepare dyes from citraconic acid in the same manner as with itaconic acid previously described (Dhar and Dutt, this *Volume*, p. 247), with a view to a systematic determination and comparison of the absorption spectra of the two series of dyestuffs so as to obtain conclusions which can be fitted into the 'Theory of colour on the basis of molecular strain' advanced by one of the present authors (Dutt, *J. Chem. Soc.*, 1926, **129**, 1871; Dutt, this *Volume*, p. 99).

Citraconic anhydride differs from itaconic anhydride by the position of a double linkage, which, in the former case, is included in a ring system, while in the latter case it belongs to a side chain. It was established by Dutt and Thorpe (*J. Chem. Soc.*, 1921, **125**, 2521) that in the cases of the dialkyl substituted succinic acids, the corresponding fluoresceins have got the following constitution :—
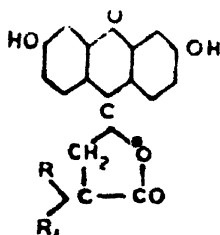
In the case of the fluoresceins of phenyl-succinic acid and methyl-succinic acid, similar constitution was also arrived at by Dutt (unpublished work). Hence from analogy it will be evident that the

structures of resorcinol-itaconein and resorcinol-citraconein are as follows :—
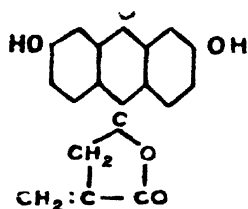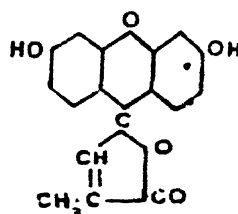
Resorcinol-itaconein.   Resorcinol-citraconein.

Hence when these substances assume quinonoid structures by solution in alkali, their configurations become as follows :—
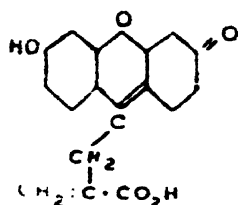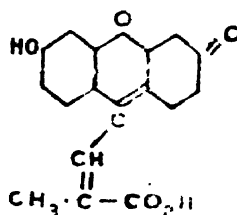
Resorcinol-itaconein.   Resorcinol-citraconein.

In the above structures the main source of strain is the quinonoid nucleus. Therefore according to the theory of colour, which has been advanced by one of the present authors, any other source of strain besides that will intensify the colour if it is in juxtaposition to the latter. In the two structures of fluoresceins given above it will be seen that the double bond corresponding to the aliphatic acid portion of the molecule is nearer to the quinonoid linkage in the case of resorcinol-citraconein, while in the case of resorcinol-itaconein it is one position further off. This will account for the fact that the absorption maxima of resorcinol-citraconein is slightly greater than that of resorcinol-itaconein. In a systematic comparison of the absorption maxima of the two series of dyestuffs, it has also been found that, in general, dyes derived from citraconic acid are always more absorptive than the corresponding dyes derived from itaconic acid. In the table of absorption maxima which has been appended it will be found that the only exceptional case in this connection is hexabromo-resorcinol-itaconein, which is slightly more

absorptive than tetrabromo-resorcinol-citraconein. But this can be easily accounted for by the presence in the former of two extra bromine atoms.

Phenol-citraconein has already been prepared and described by Krishna and Pope (*J. Chem. Soc.*, 1921, **119**, 280). With the exception of this no other dyestuffs have been obtained from citraconic acid by condensation with aromatic amino or hydroxy compounds. The following aromatic amino and hydroxy compounds have therefore been condensed with citraconic acid and the corresponding dyestuff obtained :—resorcinol, catechol, phloroglucinol, pyrogallol and *m*-diethylamidophenol. The compound with resorcinol has also been brominated and the corresponding tetra-bromo compound obtained.

EXPERIMENTAL.

The condensations of citraconic acid with aromatic amino and hydroxy compounds have been effected exactly in the same way as in the cases of the corresponding itaconeins (Dhar and Dutt, *loc. cit.*). The results are summarised below.

The Citraconeins.

Name.	Appearance.	M.p.	Colour in alkali.	Colour of fluorescence.	Analysis (calc. % in brackets).
Phenol-	... Light yellow prisms	160°	Pinkish red	...	C, 72·11(72·34) H, 4·7 (4·9)
Resorcinol-	... Yellow needles	217°	Orange red	..	H, 4·2 (4·0)
Phloroglucinol-	... ,,	Above 290°	Deep red	...	C, 61·75(62·19) H, 3·6 (3·6)
Catechol-	... Colourless prisms	260°	Pink	...	C, 68·71(68·91) H, 4·4 (4·0)
Pyrogallol-	... Dark brown needles	230°	Brown	...	C, 62·02(62·19) H, 3·9 (3·6)
Tetrabromo-resorcinol-	... Dark red needles	190°	Deep pink	Yellow	Br, 52·6 (52·2(
m-Diethylamido-phenol-	... Reddish violet prisms	95°	Bluish red	Yellowish brown	N, 8·0 (7·8)

Absorption Maxima of the Citraconeins and the Itaconeins.

C=Citraconein;   I=Itaconein.   Figures   indicate   approximate wave-lengths.

	Phenol-C.	Phenol-I.	Resor-cinol-C.	Resor-cinol-I.	Tetra-bromo-resor-cinol-C.	Hexa-bromo-resor-cinol-I.
In alcohol	4270	4290	1870	4830	5450	5480
Do, with KOH	5530	5410	4940	4880	5190	5610

	m-Diethylamidophenol-C.	m-Diethylamidophenol-I.
In alcohol	5540	5460
Do, with HCl	5560	5470

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Thiodiazines. Part V.

By Prafulla Kumar Bose and Dhirendra Chandra Ray-Chaudhury.

It has been shown by one of us (Bose, *J. Indian Chem. Soc.,* 1924, **1**, 50; *ibid*, 1925, **2**, 25) that thiosemicarbazide and 4-substituted thiosemicarbazides readily condense with ω-bromacetophenone to give rise to 1:3:4-thiodiazine derivatives, the system taking part being -C(SH):N.NH and BrCH₂CO-. The present investigation was undertaken with a view to examine if 2:4-disubstituted thiosemicarbazides, RNH.CS.N(R')NH, or RN=C(SH).NR'.NH, which contain the necessary reactive groups for the thiodiazine-ring formation would also condense in a similar way with halogenated ketones to yield thiodiazines of the type (I) thus :

$$\text{RN:C(SH).NR'.NH}_2 + \text{XCH}_2\text{COR''} \longrightarrow \quad \text{RN=C} \Big\langle {}^{\text{NR'—NH}}_{\text{S—CH}} \Big\rangle \text{C·R·}$$

(X = Halogen).   (I)
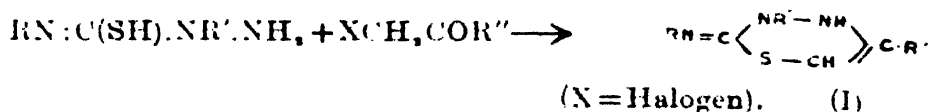
This expectation has been amply realised. In the present investigation we have employed monochloracetone, ω-bromacetophenone and *p*-methyl-ω-bromacetophenone on the one hand and 2:4-diphenyl, 2-phenyl-4-*p*-tolyl, 2-phenyl-4-*o*-tolyl, 2-phenyl-4-*m*-tolyl, 2-*p*-tolyl-4-phenyl, 2 *p*-tolyl-4-*o*-tolyl, 2:4-di-*p*-tolyl, 2-*p*-tolyl-4-*o*-anisyl, 2-*p*-tolyl-4-*m*-tolyl, and 2-*m*-tolyl-4-phenyl-thiosemicarbazides on the other; of these 2-phenyl-4-*m*-tolyl. 2-*p*-tolyl-4-*o*-anisyl, and 2-*p* tolyl-4-*m*-tolyl thiosemicarbazides appear to be new.

The reaction in all cases can be brought about by heating for a short time equimolecular quantities of the reactants in dry alcohol. Alcohol may also be replaced by acetic acid or pyridine. The use of the last solvent as a medium in the above condensation is rather restricted as some of 2:4-disubstituted thiosemicarbazides easily undergo conversion into the 1:4-variety in this solvent, the halogenated ketone at the same time reacts with pyridine or with 1:4-compounds to give uncrystallisable products. If however the 2:4-compound be not very susceptible to the 1:4-transformation in this solvent, the halogenated ketone reacts chiefly with the thiosemicarbazide.

The thiodiazines thus obtained are stable crystalline substances most of which are colourless. They are rather weak bases since the hydrochlorides or hydrobromides readily hydrolyse in aqueous solution and if sufficient water be present, the base is precipitated. They are not desulphurised when boiled with freshly precipitated mercuric oxide or with alkaline lead acetate solution.

Attempts to acetylate these compounds by means of acetic anhydride or acetyl chloride in pyridine solution were fruitless. The thiodiazines also failed to react with phenyl mustard oil when heated in acetone solution for 8 hours. It is difficult at this stage to state definitely whether the non-reactivity of the imino hydrogen atom is to be attributed to steric influence of the adjoining radicles on either side of the NH group in position 4 or to the alternate configuration (II).

$$RN=C \left< \begin{matrix} NR'-N \\ S-CH_2 \end{matrix} \right> C \cdot R \qquad (II)$$

1:4-Diphenyl-thiosemicarbazide reacts with ω-bromacetophenone in boiling alcoholic solution but from the resulting tarry product the expected thiodiazine (III) could not be isolated.

$$Ph \cdot NH \cdot C \left< \begin{matrix} N-NPh \\ S-CH \end{matrix} \right> C \cdot Ph$$
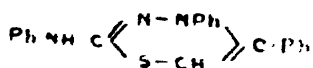
(III)

If however equivalent quantities of the reactants are suspended in alcohol and left at the room temperature for several months, condensation takes place very slowly, and the resulting product is found to be identical with that derived from 2:4-diphenyl thiosemicarbazide, namely 2-phenylimino-2:3-dihydro-3:5-diphenyl-1:3:4-thiodiazine.

Since the 1:4-compound and ω-bromacetophenone do not react to yield the expected thiodiazine (III), the conclusion that 1:4-diphenyl thiosemicarbazide undergoes conversion into the 2·4-variety appears reasonable.

It had however been noticed that 1:4-diphenyl thiosemicarbazide decomposes into phenyl mustard oil and phenylhydrazine

hydrochloride when the thiosemicarbazide is boiled with hydrochloric acid, thus:

$$PhNH.CS.NH.NHPh + HCl = PhNCS + PhNH.NH_2Cl.$$
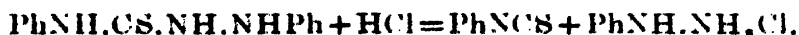
Busch (*Ber.*, 1909, **42**, 4596) has, moreover, noticed that alkyl or aryl *isothiocyanates* combine with salts of substituted hydrazines to yield 2:4-disubstituted thiosemicarbazides even at the temperature of a boiling water-bath. The above observations consequently lead us to suppose that in the present case 1:4-diphenyl-thiosemicarbazide slowly splits up into phenyl mustard oil and phenyl hydrazine hydrobromide under the influence of hydrobromic acid liberated by the action of bromacetophenone on a portion of 1:4-diphenyl thiosemicarbazide. The mustard oil and hydrazine hydrobromide then combine to form 2:4-diphenyl thiosemicarbazide which reacts with bromacetophenone in the usual way.

<div align="center">EXPERIMENTAL.</div>

2-Phenylimino-2:3-dihydro-3:5-diphenyl-1:3:4-thiodiazine.

One mol. proportion of 2:4-diphenyl thiosemicarbazide (1·2 g.) and 1 mol. proportion of ω-bromacetophenone (1 g.) were shaken with 10 c.c. of anhydrous alcohol in a flask. Heat was evolved and the thiosemicarbazide passed into solution. The flask was heated for a minute on the water-bath to complete the reaction. The solution was then concentrated and 2 c.c. of pyridine and a little water were added when the base crystallised out. This was collected and washed with dilute alcohol (yield 67 per cent.). The base was dissolved in a mixture of alcohol and pyridine, boiled with animal charcoal, filtered and cooled. The pale yellow needles thus obtained were recrystallised from acetone; m.p. 184°. (Found. N, 12·19; S, 9·18. $C_{,,}H_{,,}N_{,}S$ requires N, 12·24; S, 9·33 per cent.). The base is easily soluble in benzene, chloroform, carbon disulphide and pyridine; moderately so in ether and acetone and sparingly in alcohol.

1:4-Diphenylthiosemicarbazide and ω-Bromacetophenone : Formation of 2-Phenylimino-2:3-dihydro-3:5-diphenyl-1:3:4-thiodiazine.

Molecular proportions of 1:4-diphenyl thiosemicarbazide and bromacetophenone were suspended in anhydrous alcohol in a flask which was tightly corked. The flask was kept aside at the room

temperature. The thiosemicarbazide passed into solution very gradually. The colour of the solution turned green in about two months. In 5 to 6 months the colour changed to reddish brown and a crystalline precipitate appeared. This was collected after a further period of 6 months. The mother-liquor, on concentration, produced a second crop of pale yellow crystals. The two crops were found to be identical. They crystallised from a mixture of pyridine and alcohol in pale yellow needles, m. p. 184 . The identity of this product with 2-phenylimino-2:3-dihydro-3:5-diphenyl-1:3:4-thiodiazine was established by usual tests, as also by analysis. (Found: N, 12·33. $C_{21}H_{17}N_3S$ requires N, 12·24 per cent.).

If the condensation of the 1:4-compound with the bromoketone is carried out on the water-bath in alcohol or pyridine, a non-crystallisable product is obtained.

2-p-*Tolylimino*-2:3-*dihydro*-3:5-*diphenyl*-1:3:4-*thiodiazine*.

2-Phenyl-4-*p*-tolyl thiosemicarbazide (1·7 g.), bromacetophenone (1·3 g.) and anhydrous alcohol (12 c.c.) were shaken for some time when the components passed into solution with evolution of heat. The solution was then heated on the water-bath for a minute or two when the hydrobromide of the condensation product separated out (yield 84 per cent.). The hydrobromide was dissolved in alcohol and aqueous ammonia added to precipitate the free base. When crystallised from acetone using animal charcoal as a decoloriser, the thiodiazine formed colourless crystals, m. p. 166 . (Found: N, 11·93. $C_{22}H_{19}N_3S$ requires N, 11·76 per cent.).

2-o-*Tolylimino*-2:3-*dihydro*-3:5-*diphenyl*-1:3:4-*thiodiazine*.

The method of preparation is practically the same as for the preceding compound, 2-phenyl-4-*o*-tolyl thiosemicarbazide being employed in this case. The hydrobromide is however more soluble.

The base separated from acetone in needles, m. p. 131-32 , (Found: N, 11·74. $C_{22}H_{19}N_3S$ requires N, 11·76 per cent.).

It is highly soluble in benzene, chloroform, glacial acetic acid or pyridine, but moderately so in alcohol or acetone.

If the reaction is carried out in pyridine, the above condensation product is not obtained and the semicarbazide is simply transformed into the isomeric 1-phenyl-4-*o*-tolyl thiosemicarbazide.

2-*Phenyl-4-m-tolyl-thiosemicarbazide*.

Phenyl hydrazine (1·1 g.) dissolved in 30 c.c. of alcohol and a few drops of glacial acetic acid was cooled in ice. *m*-Tolyl mustard oil (1·6 g.) also dissolved in a little alcohol was added drop by drop with constant shaking. Colourless crystals appeared after a short time. These were freed from the mother-liquor, washed with 20 per cent. alcohol and finally with ether and dried at the ordinary temperature; m. p. 123°. (Found: S, 12·56. $C_{14}H_{15}N_3S$ requires S, 12·46 per cent.). In presence of warm solvents it is converted into the 1:4-variety, m. p. 173°.

2-m-*Tolylimino-2* : 3-*dihydro-3*:5-*diphenyl-1* : 3 : 4-*thiodiazine*.

2-Phenyl-4-*m*-tolyl thiosemicarbazide (1·7 g.) and ω-bromacetophenone (1·3 g.) were shaken with 1·5 c.c. of glacial acetic acid. Heat was evolved and the components went into solution. The solution was heated on the water-bath for a while, cooled and diluted with water when a semi-solid mass was obtained. This was washed several times with water and finally with 40 per cent. alcohol. The crystalline residue was recrystallised from alcohol after usual treatment with animal charcoal when colourless needles, m. p. 119-20° were obtained. (Found: N, 11·82 ; S, 8·54. $C_{22}H_{19}N_3S$ requires N, 11·76; S, 8·90 per cent.).

The substance dissolves easily in pyridine, chloroform, benzene, or acetone but moderately in alcohol.

The condensation does not take place in pyridine; a conversion of 2 : 4- into the 1 : 4-compound takes place.

2-*Phenylimino-2* : 3-*dihydro-3-p-tolyl-5-phenyl-1* : 3 : 4-*thiodiazine*.

On shaking 2-*p*-tolyl-4-phenyl thiosemicarbazide (1·3 g.) and of ω-bromacetophenone (1 g.) in pyridine a clear solution was obtained and heat developed. The reaction was completed on the water-bath and water added when the base crystallised out. It was recrystallised from dilute pyridine, after treatment with animal charcoal, as colourless, rectangular plates, m. p. 122-23°. (Found: N, 12·06. $C_{22}H_{19}N_3S$ requires N, 11·76 per cent.). It is highly soluble in benzene and carbon disulphide, moderately so in acetone and pyridine but sparingly soluble in alcohol.

2-m-*Tolylimino*-2 : 3-*dihydro*-3-p-*tolyl*-5-*phenyl*-1 : 3 : 4-*thiodiazine*.

The condensation product (yield 89 per cent.) was obtained in a similar manner from 2-p-tolyl-4-o-tolyl thiosemicarbazide and bromacetophenone. For purification an alcoholic solution of the base was boiled with animal charcoal, filtered and cooled when it separated in colourless needles, m. p. 112°. (Found : N, 11·39. $C_{22} H_{21} N_3$ S requires N, 11·32 per cent.). The compound is easily soluble in carbon disulphide and benzene, but moderately so in alcohol, acetone or pyridine.

2-p-*Tolylimino*-2 : 3-*dihydro*-3-p-*tolyl*-5-*phenyl*-1 : 3 : 4-*thiodiazine*.

2-p-tolylimino-2 : 3-dihydro-3-p-tolyl-5-phenyl-1 : 3 : 4-thiodiazine, obtained as above from 2 : 4-di-p-tolyl thiosemicarbazide and ω-bromacetophenone in an yield of 84 per cent., formed colourless crystals, m. p. 145-46°. (Found : N, 11·31. $C_{22} H_{21} N_3$ S requires N, 11·32 per cent.). It is moderately soluble in benzene, glacial acetic acid, alcohol or pyridine.

2-p-*Tolyl*-4-o-*anisyl thiosemicarbazide*.

The thiosemicarbazide was obtained from p-tolyl hydrazine and o-anisyl mustard oil by a process similar to that employed for 2-phenyl-4-m-tolyl thiosemicarbazide. It crystallised from benzene in colourless crystals on the addition of ligroin. (Found : S, 11·54. $C_{15} H_{17} N_3$ S requires S, 11·4 per cent.).

2-o-*Anisylimino*-2 : 3-*dihydro*-3-p-*tolyl*-5-*phenyl*-1 : 3 : 4-*thiodiazine*.

2-p-Tolyl-4-o-anisyl thiosemicarbazide (1·4 g.) and ω-bromacetophenone (1 g) were heated with about 10 c.c. of alcohol on the water-bath for five minutes. On cooling, the hydrobromide of the condensation product crystallised out. This was dissolved in dilute alcohol and treated with aqueous ammonia when the base was precipitated (yield 94 per cent.). On recrystallisation from alcohol it formed colourless needles melting at 109°. (Found : N, 11·08. $C_{23} H_{21} N_3$ SO requires N, 10·85 per cent.). The thiodiazine is highly soluble in pyridine or acetone, moderately in glacial acetic acid and alcohol and insoluble in ether. The above condensation could also be effected in pyridine solution.

2-p-*Tolyl*-4-m-*tolyl thiosemicarbazide.*

The thiosemicarbazide was obtained from p-tolyl hydrazine and m-tolyl mustard oil in cold alcoholic solution. The colourless crystals were freed from the mother-liquor by washing with 20 per cent. alcohol and finally with ether. It was dried in air, m. p. 151°. (Found : S, 12·24. $C_{15}H_{17}N_3S$ requires N, 11·80 per cent.). It passes into the 1 : 4-variety (m. p. 167°) when heated with any solvent.

2-m-*Tolylimino*-2 : 3-*dihydro*-3-p-*tolyl*-5-*phenyl*-1 : 3 : 4-*thiodiazine.*

2-p-Tolyl-4-m-tolyl-thiosemicarbazide (1·4 g.) and ω-bromacetophenone (1 g.) were shaken with 15 c.c. of glacial acetic acid for about 30 minutes when the substances passed into solution with slight rise of temperature. The condensation product when recrystallised from a mixture of alcohol and pyridine using animal charcoal formed prisms melting at 106-107°. (Found : N, 11·39. $C_{23}H_{21}N_3$ requires N, 11·32 per cent.). It dissolves easily in benzene, chloroform or acetone, moderately so in pyridine or glacial acetic acid and sparingly so in alcohol. Condensation, however, did not take place in pyridine solution.

2-*Phenylimino*-2 : 3-*dihydro*-3-m-*tolyl*-5-*phenyl*-1 : 3 : 4-*thiodiazine.*

A mixture of 2-m-tolyl-4-phenyl thiosemicarbazide (1·2 g) and bromacetophenone (1 g.) was dissolved in glacial acetic acid at ordinary temperature and allowed to stand for 3 hours. It was then heated on the water-bath for ten minutes and diluted with much water. The product was purified as before. From a mixture of alcohol and pyridine it was obtained as colourless prisms melting at 153° (yield 60 per cent.). (Found : N, 11·56. $C_{22}H_{19}N_3S$ requires N, 11·76 per cent.).

It is easily soluble in benzene, carbon disulphide and pyridine, but sparingly so in alcohol.

As 2-m-tolyl-4-phenyl thiosemicarbazide is unstable, the yield of the thiodiazine is very much diminished if the solution is heated just after the addition of the reactants.

2-*Phenylimino*-2 : 3-*dihydro*-3-*phenyl*-5-p-*tolyl*-1 : 3 : 4-*thiodiazine.*

The procedure is practically the same as adopted for the preparation of 2-phenylimino-2 : 3-dihydro-3 : 5-diphenyl-1 : 3 : 4-

thiodiazine, with the difference that *p*-methyl-ω-bromacetophenone was used in this case. From acetone the base separated in yellow prisms melting at 165°. (Found : N, 11·82. $C_{23}H_{18}N_3$ S requires N, 11·76 per cent.).

It is easily soluble in benzene, carbon disulphide, glacial acetic acid and pyridine but moderately so in acetone and sparingly in alcohol.

2-*Phenylimino*-2 : 3-*dihydro*-3-m-*tolyl*-5-p-*tolyl*-1 : 3 : 4-*thiodiazine*.

2-*m*-Tolyl-4-phenyl thiosemicarbazide (1·2 g.) and *p*-methyl-ω-bromacetophenone (1·1 g.) were dissolved in anhydrous alcohol without application of heat. The solution was kept overnight at the room temperature and finally heated on the water-bath for a short time and allowed to cool. Dilute pyridine was added when the free base crystallised out. From alcohol the thiodiazine was obtained in colourless crystals melting at 136°. (Found : N, 11·32. $C_{23}H_{21}N_3$ S requires N, 11·32 per cent.).

It is highly soluble in benzene, chloroform, acetone, pyridine but moderately so in alcohol.

2-p-*Tolylimino*-2 : 3-*dihydro*-3-*phenyl*-5-p-*tolyl*-1 : 3 : 4-*thiodiazine*.

The condensation was carried out as usual with 2-phenyl-4-*p*-tolyl thiosemicarbazide and *p*-methyl-ω-bromacetopheone. The base was liberated using pyridine and was crystallised from acetone in yellow needles, m. p. 180°. (Found : N, 11·43. $C_{23}H_{21}N_3$ S requires N, 11·32 per cent.). The thiodiazine readily dissolves in benzene, carbon disulphide, ether, pyridine, moderately in acetone and sparingly in alcohol.

2-*Phenylimino*-2 : 3-*dihydro*-3-*phenyl*-5-*methyl*-1 : 3 : 4-*thiodiazine*.

2 : 4-Diphenyl thiosemicarbazide (2·4 g.) and monochlor-acetone (1 g.) were heated with 15 c.c. of anhydrous alcohol for about 15 minutes on the water-bath. The solution was concentrated and dilute pyridine added to isolate the free base (yield 65 per cent.). It crystallised from alcohol in colourless shining plates melting at 153-54°. (Found : C, 68·34 ; H, 5·65. $C_{16}H_{15}N_3S$ requires C, 68·32 ; H, 5·33 per cent.).

Our sincere thanks are due to Sir P. C. Ráy for his kind interest in the above investigation.

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A Theory of Colour on the Basis of Molecular Strain. Part III. Decomposition of Dyes by the Influence of Solar Radiation.

By Kali Krishna Barat and Sikhibhushan Dutt.

In two previous communications by one of the present authors (Dutt, *J. Chem. Soc.*, 1926, **129**, 1171 ; and Dutt, this *Volume*, p. 99) a general theory of colour on the basis of molecular strain has been elaborated whereby it has been shown that the intensity of colour or the absorption maxima of dyestuffs are in direct proportion to the amount of relative strain contained within the molecule. In this paper an attempt has been made to find out whether the reverse of such a statement will hold good, that is to say, whether the relative strain within the molecules of dyestuffs is in direct proportion to their absorption maxima. And this has been achieved by a direct comparison of their rate of decomposition under the influence of solar radiation.

In a previous paper (Dutt, this *Journal*, *loc. cit.*) it has been shown that amount of relative strain within the molecule of substances can be ascertained by the rapidity with which they undergo decomposition under the influence of various chemical reagents with formation of less strained compounds. Some very simple instances like stilbene, benzylidene aniline, azobenzene, benzophenone and nitrosobenzene were taken and the action of nascent hydrogen on these substances were examined. In each case a hydrogenated, *i.e.*, a less strained compound was formed, and it was found on examination and comparison of the quantity of the resultant products that the amount of calculated strain was in direct proportion to the reactivity of the substances under the influence of nascent hydrogen. Innumerable instances of similar nature can be given in which the conclusions drawn from the foregoing experiments can be applied with success. Looking through the vast number of compounds belonging to organic chemistry, it is almost invariably found that great reactivity or instability means great molecular strain.

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Now it has been a well-known fact for quite a long time that the great majority of the dyestuffs under the influence of sunlight tend to bleach away with the formation of colourless products. From the point of view of the theory of colour that has been advanced by one of the present authors, this is a very interesting case in which strained compounds gradually lose their molecular strain under the influence of an external stimulus i.e., solar radiation by the chemical process of either oxidation, reduction, hydration, condensation or hydrolysis. The affair bears some analogy with the detonation of such highly strained compounds as the halides of nitrogen under the influence of compression waves into their elements, or the spontaneous combustion of the highly strained ketons under the influence of sunlight into carbon dioxide and water. When a dyestuff in aqueous solution becomes bleached in presence of sunlight into colourless products, but remains absolutely unchanged in the dark, it becomes quite evident that the sunlight or the radiant energy of the sun acts only as a stimulus to liberate the potential energy contained within the highly strained molecule in the same way as a detonator acts with explosive compounds.

From these it will be seen that the greater the amount of strain within the molecule of a dyestuff, the more easily and quickly it will tend to bleach away into colourless products under the influence of solar radiation. In other words, the more intensely coloured dyestuffs, e.g., the green, blue and violet ones will decompose much more readily than the less coloured ones, e.g., the yellow, orange and red dyestuffs. In fact such expectation has been realised with very few exceptions.* From the experiments that have been carried out in this laboratory it has been found in general that rate of decomposition of dyestuffs is in the following increasing order of magnitude—yellow, orange, red, violet, blue and green. The green, blue and violet dyes are the most fugitive, while the yellow and orange dyes are the most stable.

The total radiant energy of sunlight during the course of these experiments has been ascertained from time to time by the micro-radiometer method, and has been found to remain almost constant,

* The cases of eosin and erythrosin are anomalous probably on account of the large amount of halogen that is contained within their molecule and the ease with which they are liberated in the form of hydrogen halides with consequent decomposition of the whole molecule. The case of acid green (GG) is also anomalous probably due to the great complexity of the molecule and the large area over which the strain is distributed.

the average value being about 4.6×10^{11} ergs per sq. cm. per second. But though of course the figure for the total radiation of the sun is not the same as for the active radiation which is really responsible for the decomposition of the dyestuffs, yet the total and the active radiations must bear a ratio to one another, which must have been constant during the series of experiments that were performed. Hence these experiments were strictly comparative. The following dyestuffs were examined:—

(1) *Green*—Malachite green, Ethyl green, Bindschedlers green, Acid green, Brilliant green.

(2) *Blue*—Methylene blue, Indigo carmine, Meldola's blue, Nile blue.

(8) *Violet*—Crystal violet, Gentian violet, Methyl violet.

(4) *Red*—Erythrosine, Safranine, Eosine, Rhodamine, Fuchsine, Congo red.

(5) *Orange*—Methyl orange, Orange II, Tropaeoline (OO).

(6) *Yellow*—Acridine yellow, Uranine, Naphthol yellow, Picric acid.

EXPERIMENTAL.

Specially purified samples of dyestuffs were obtained by successive recrystallisations of the purest available commercial specimens for a number of times until their melting points were constant or there were no changes noticeable in their absorption spectra. Solutions of these dyes in water were made up to a certain strength (N/ 10,000 in most cases) and the solutions exposed to sunlight in air-tight bottles made of specially transparent and colourless glass. The absorption spectra of these solutions during their exposure to sunlight were recorded at regular intervals. The instrument used was a quartz spectrograph of about 5 inches dispersion, a copper arc in conjunction with a 4 inch condenser being used as the illuminant.

In connection with these series of absorption spectra, it should be noted that apart from the absorption maxima, the width of the band is of great importance. In many of the cases the absorption maxima varies but little from the point of exposure to sunlight to that of the complete bleaching away of the dye solution under the influence of solar radiation, while during that interval the width of the band varies considerably. The net effect of sunlight is therefore

practically the same as that of the gradual dilution of the dye solution until its colour becomes invisible. Hence it is apparent that, in general, sunlight decomposes dyestuffs directly into colourless products with very little formation of less coloured compounds having different absorption maxima.

For the sake of convenience the absorption spectra of various dyes in course of their exposure to sunlight have been summarised into tabular forms.

[Figures indicate approximate wave-lengths of absorption maxima.

Figures within brackets indicate the maximum width of the absorption band in Angström units.]

GREEN DYESTUFFS.

Bindschedlers Green.

		λ
Before exposure	...	7310 (2000)
10th hour	...	6250 (1800)
20th ,,	...	5875 (1500)
30th ,,	...	Bleached.

Malachite Green.

		λ
Before exposure	...	6190 (1900)
20th hour	...	6000 (1650)
40th ,,	...	5960 (1200)
50th ,,	...	Bleached.

Brilliant Green.

		λ
Before exposure	...	6250 (3000)
20th hour	...	6230 (1700)
40th ,,	...	5540 (1800)
50th ,,	...	Bleached.

Ethyl Green.

		λ
Before exposure	...	6150 (2150)
20th hour	...	6125 (1650)
40th ,,	...	6050 (1550)
60th ,,	...	5850 (1150)
80th ,,	...	Bleached.

Acid Green.

		λ
Before exposure	...	6450 (2850)
60th hour	...	6075 (1550)
120th ,,	...	6000 (1450)
250th ,,	...	6000 (1156)
850th ,,	...	Bleached.

BLUE DYESTUFFS.

Methylene Blue.

		λ
Before exposure	...	6650 (3000)
80th hour	...	6070 (2600)
60th ,,	...	6000 (2000)
75th ,,	...	Bleached.

Indigo-carmine.

		λ
Before exposure	...	6090 (1550)
20th hour	...	6090 (1550)
40th ,,	...	5550 (450)
50th ,,	...	Bleached.

Meldola's Blue.

	λ
Before exposure ...	6060 (1600)
60th hour ...	6040 (1500)
120th ,, ...	6040 (1500)
200th ,, ...	5900 (1000)
250th ,, ...	Bleached.

Nile Blue A

	λ
Before exposure ...	6040 (2250)
30th hour ...	6015 (2200)
60th ,, ...	6000 (1900)
90th ,, ...	6000 (1500)
120th ,, ...	Bleached.

VIOLET DYESTUFFS.

Methyl Violet.

	λ
Before exposure ...	5530 (2010)
20th hour ...	5510 (1900)
40th ,, ...	5250 (1510)
50th ,, ...	Bleached.

Gentian Violet.

	λ
Before exposure ...	5650 (2500)
20th hour ...	5450 (2350)
40th ,, ...	5400 (410)
50th ,, ...	Bleached.

Crystal Violet.

	λ
Before exposure ...	5990 (2440)
20th hour ...	5930 (2300)
40th ,, ...	5580 (2070)
60th ,, ...	5560 (850)
70th ,, ...	Bleached.

RED DYESTUFFS.

Erythrosin.

	λ
Before exposure ...	5460 (1530)
10th hour ...	5100 (500)
20th ,, ...	Bleached.

Eosin.

	λ
Before exposure ...	5210 (1500)
20th hour ...	5210 (1500)
40th ,, ...	5050 (1100)
60th ,, ...	Bleached.

Safranine T.

	λ
Before exposure ...	5250 (1880)
20th hour ...	5200 (1100)
30th ,, ...	5200 (900)
40th ,, ...	5150 (800)
50th ,, ...	Bleached.

Fuchsine.

	λ
Before exposure ...	5450 (2030)
25th hour ...	5450 (2030)
50th ,, ...	5450 (1960)
100th ,, ...	5300 (1250)
125th ,, ...	Bleached.

Rhodamine B.			Congo red.		
		λ			λ
Before exposure	...	5540 (1250)	Before exposure	...	5240 (2300)
100th hour	...	5580 (1250)	100th hour	...	5240 (2300)
150th ,,	...	5520 (1200)	150th ,,	...	5100 (2000)
200th ,,	...	5280 (980)	200th ,,	...	4850 (650)
250th ,,	...	Bleached.	250th ,,	...	Bleached.

ORANGE DYESTUFFS.

Methyl Orange.			Orange II.		
		λ			λ
Before exposure	...	5040 (1200)	Before exposure	...	5040 (1200)
100th hour	...	4970 (1050)	100th hour	...	4970 (1050)
450th ,,	...	4850 (950)	300th ,,	...	4920 (950)
650th ,,	...	4850 (950)	700th ,,	...	4800 (700)
850th ,,	...	Bleached.	900th ,,	...	Bleached.

Tropeolin OO.		
		λ
Before exposure	...	5000 (1100)
100th hour	...	4970 (1050)
300th ,,	...	4920 (950)
700th ,,	...	4900 (900)
900th ,,	...	Bleached.

YELLOW DYESTUFFS.

Acridine Yellow.			Uranin.		
		λ			λ
Before exposure	...	4100 (1100)	Before exposure	...	4940 (1260)
50th hour	...	4100 (1100)	100th hour	...	4650 (840)
100th ,,	...	3800 (500)	150th ,,	...	4600 (380)
125th ,,	...	3800 (500)	175th ,,	...	4600 (300)
150th ,,	...	Bleached.	200th ,.	...	Bleached.

Naphthol Yellow S.			Picric Acid.		
		λ			λ
Before exposure	...	4350 (1450)	Before exposure	...	4200 (1300)
100th hour	...	4350 (1450)	100th hour	...	4130 (1260)
300th ,,	...	4350 (1450)	400th ,,	...	4130 (1260)
500th ,,	...	4100 (1200)	800th ,,	...	4130 (1260)
600th ,,	...	Bleached.	1000th ,,	...	Not bleached

Synthetical Experiments in the Carbazole Series.

By Basavalingaiah Lingaiah Manjunath.

The following work was undertaken with the object of synthesising a molecule composed of three benzene nuclei and two pyrrole nuclei condensed together as represented by formula I. This substance could be used as the starting point for the preparation of many interesting derivatives. Graebe and Ullmann (*Annalen*, 1896, 291, 16) synthesised carbazole by heating 1-phenylbenzotriazole, a reaction which was later used by Ullmann for preparing several derivatives of carbazole, while 8-carboline and 5-carboline have been prepared in a similar way (Lawson, Perkin and Robinson, *J. Chem. Soc.*, 1924, 125, 6 6; Robinson and Thornley, *ibid*, 1924, 125, 2169). It was thought that it might be possible to construct an indole nucleus upon carbazole in this way from a 1-*carbazylbenzotriazole*. With the object of preparing 1-carbazylbenzotriazole attempts were made to condense 3-aminocarbazole (II) with o-chloronitrobenzene, o-bromonitrobenzene, and m-nitro-p-chlorbenzoic acid, but without success. It was also noticed that 8-bromocarbazole (Ciamician and Silber, *Gazzetta*, 1882, 12, 276) could not be condensed with o-nitraniline, o-phenylenediamine or even methyl amine. Further it was not possible to obtain from it the Grignard compound. It was found, however, that 8-aminocarbazole condensed with 2:4-dinitrochlorbenzene to give 3-(2′:4′-dinitroanilino)-carbazole (III), which was converted successively into 3-(2′-*amino*-4-
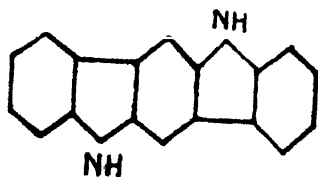
(I)
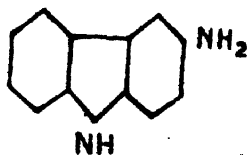
(II)
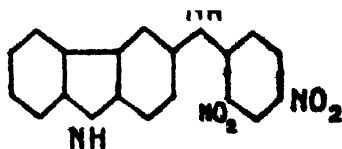
(III)

nitroanilino)-*carbazole*, 1:8-*carbazyl*-5-*nitrobenzotriazole* and 1:8-*carbazyl*-5-*aminobenzotriazole* (IV). Attempts to eliminate nitrogen

from the two compounds failed, although Ullmann synthesised
2-aminocarbazole by heating 1-phenyl-5-aminobenzotriazole (V).

(IV)   (V)
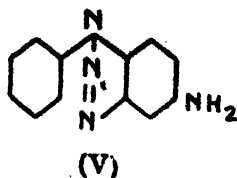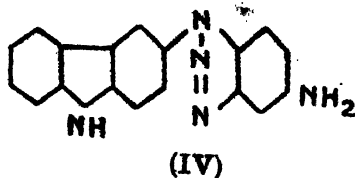
A series of experiments was then made with the object of
preparing *o-phenylene*-1 : 1'-*dibenzotriazole*, from which it was hoped
that the desired nucleus could be obtained on heating by the loss
of two molecules of nitrogen. It was found that 4 : 6-diamino-1 : 3-
dianilinobenzene (VI) (Nietzki and Schelder, *Ber.*, 1897, 30, 1668),
on treatment with nitrous acid, gave a green, uncrystallisable
product, which reacted with aniline to form azophenine. Neverthe-
less, *p*-dibromobenzene was condensed with *o*-nitraniline and the
product was reduced to p-*di-o-aminoanilinobenzene* (VII), which gave
p-*phenylene*-1 : 1'-*dibenzotriazole* (VIII) with nitrous acid. This
substance decomposed into resinous products on heating.

(VI)   (VII)

(VIII)   (IX)
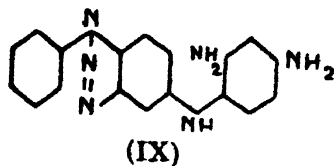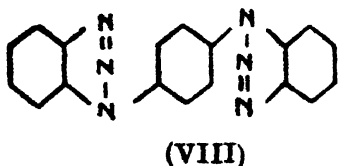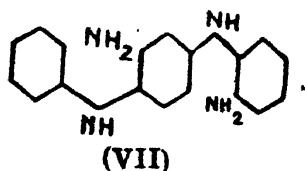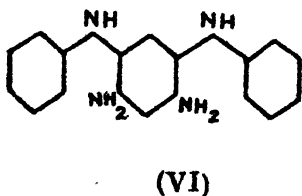
The difficulty of adding an indole nucleus to carbazole suggested
an investigation of the possibility of building some other hetero-
cyclic structure on the substance. Phenazine compounds have been
prepared by oxidising derivatives of 2-aminodiphenylamine (Fischer
and Heiler, *Ber.*, 1893, 26, 388; Fischer, *Ber.*, 1896, 29, 1878;
Nietzki and Simcr, *Ber.*, 1895, 28, 2974), and, with the object of
carrying out a similar reaction, 3-(2' : 4'-dinitroanilino)-carbazole (III)
has been reduced to the corresponding *diaminoanilinocarbazole*, but
this substance, on oxidation, gave products which could not be

purified. With a similar object in view, 1-p-2':4'-*diaminoanilino-phenyl-bensotriazole* (IX) was prepared, but attempts to produce both the phenazine and the carbazole systems from this compound again failed. The extreme difficulties in the way of preparing a diamino derivative of carbazole, in which the two amino groups occupy *ortho*-positions to one another, prevented the use of such a compound as the starting point for constructing a new heterocyclic system. 2 : 7-Diaminocarbazole (Täuber, *Ber.*, 1890, **23**, 3266), has been prepared, and some of its derivatives obtained. But it was not possible to isolate a definite compound as a result of nitration.

The ordinary methods for making hydrazines fail in the case of 3-aminocarbazole (Ruff and Stein, *Ber.*, 1901, **34**, 1682), so that there is no possibility of carrying out a Fischer indole synthesis with 3-*hydrazinocarbazole*. It was not possible to prepare 3-*methylamino-carbazole* in order that its nitroso derivative could be utilised for indole formation by reducing it in the presence of *cyclo*hexanone with subsequent warming in acid solution (see Clemo, and Perkin, jun., *J. Chem. Soc.*, 1924, **125**, 1619; Linnell, and Perkin, jun., *ibid*, p. 2459). When *p* : *p'*-dinitrosodimethylphenylenediamine, (Willstätter, and Pfannenstiel, *Ber.*, 1905, **38**, 2249), m. p. 148° was similarly reduced, the nitroso groups were simultaneously eliminated. 9-Aminocarbazole (X) (Wieland, Susser and Fressel, *Annalen*, 1912, **392**, 183) has been condensed with *cyclo*hexanone, but attempts to remove ammonia from the product to give a substance of the formula (XI) were unsuccessful. It was found, however, that when 9-nitrosohexahydrocarbazole (XII) is reduced in the presence of *cyclo*hexanone by means of zinc and acetic acid and the solution subsequently warmed, 8 : 9-(1' : 2'-cyclo*hexyl*)-*tetrahydrocarbazole* (XIII) is formed.
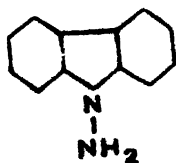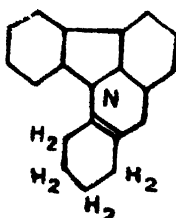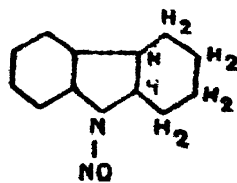
(X)　　　　　　(XI)　　　　　　(XII)

Similarly, 6-*methyl*-8 : 9-(1' : 2'-cyclo*hexyl*)-*tetrahydrocarbazole* has been obtained from 6-*methylhexahydrocarbazole*. These products behave more like tetrahydrocarbazole than like hexahydrocarbazole.

being insoluble in dilute acids and not giving definite methiodides. By electrolytic reduction 8:9-(1':2'-cyclohexyl)- hexahydrocarbazole (XIV) has been prepared, and this substance is quite basic, dissolving in dilute acids and giving a definite methiodide.
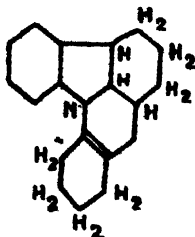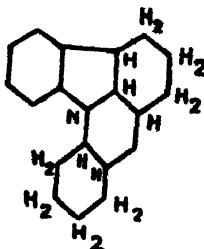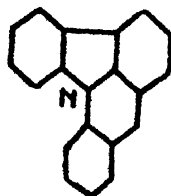
(XIII)   (XIV)   (XV)

Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 78) oxidised tetrahydrocarbazole to carbazole by heating with lead oxide while the same reaction can be carried out by heating with sulphur in quinoline solution (Perkin and Plant, *J. Chem. Soc.*, 1923, **123**, 694). Attempts to convert the compounds described above into the parent substance represented by formula (XV) by these methods were not successful, although it was found that hexahydrocarbazole could be oxidised to carbazole.

EXPERIMENTAL.

The following method was found to be the most convenient for the preparation of the comparatively large quantities of 3-aminocarbazole required for these investigations (compare D.R.P., 1913/294016 ; Ruff, and Stein, *Ber.*, 1901, **34**, 1677 ; Ziersch, *Ber.*, 1909, **42**, 3798 ; D.R.P., 1901/134983 ; Schwalbe, and Wolff, *Ber.*, 1911, **44**, 235 ; Lindemann, *Ber.*, 1924, **57**, 557). Carbazole (50 g.) was dissolved in boiling acetic acid (600 c.c.) and, while slowly cooling the solution, sodium nitrite (21 g.) was gradually added. Without further heating, nitric acid (38 c.c. of *d* 1·4) was added drop by drop with vigorous stirring, and 9-nitroso-3-nitrocarbazole separated. After half an hour the product (60 g., m. p. 164°) was collected, washed with alcohol and suspended in alcohol (600 g.). Molten, crystallised sodium sulphide (500 g.) was then added gradually, and the mixture boiled under reflux for 5 hours, during which 3-aminocarbazole separated. The alcohol was removed by distillation, the residue diluted with water and the product (40 g., m. p. 251°) was

collected and washed with ether. 8-Aminocarbazole crystallised from toluene melts at 258° when pure.

8-(2′:4′-Dinitroanilino)-carbazole (III).—8-Aminocarbazole (18 g.) was suspended in alcohol (200 c.c.) containing 2:4-dinitrochlorobenzene (20 g.), and finely powdered sodium acetate (20 g.). The mixture was boiled under reflux for two hours when a red crystalline mass separated. Excess of water was added to the cooled mixture, the precipitate collected and dried. The yield was quantitative and the crude product melted at 255°. A portion of it was recrystallised form nitrobenzene. Thin bright scarlet prisms, m. p. 258°. (Found: N, 16·0. $C_{18}H_{11}O_4N_4$ requires N, 16·1 per cent.).

8-(2′-Amino-4′-nitroanilino)-carbazole.—The dinitro compound (III) (17·4 g.) was suspended in ten times its weight of boiling alcohol. Freshly prepared hot sodium hydrogen sulphide solution (42 g. of crystallised sodium sulphide converted into the hydrosulphide by the addition of the requisite amount of conc. HCl to the fused mass), was gradually added and vigorously stirred. Care must be taken in this operation as the reaction is apt to become violent. The mixture was then boiled under reflux for two hours. On cooling and dilution the aminonitroanilino-compound separated out in quantitative yield. It was filtered and dried at 80°. The product was fairly pure and melted at 242°. A portion of it was recrystallised from xylene. Chocolate brown rectangular prisms, darken between 220° and 250° and melt at 256°-258°. (Found: N, 17·3. $C_{18}H_{14}O_2N_4$ requires N, 17·6 per cent.).

It was also possible to obtain the above compound by directly reducing the dinitro compound (III) after its formation. The compound dissolved in alcoholic hydrochloric acid with a deep red colour and was sparingly soluble in the usual organic solvents.

1:8-Carbazyl-5-nitrobenzotriazole.—A solution of the hydrochloride of the above described nitramine in alcohol was treated with a conc. solution of the requisite quantity of sodium nitrite, with vigorous stirring, at 5°. The insoluble triazole gradually separated out as a dark green precipitate. After keeping for 2 hours at 0° the mixture was filtered out and the residue dried. The yield was quantitative. Pale yellow prisms (from xylene) melting with decomposition at 288°. (Found: N, 21·1. $C_{18}H_{11}O_2N_5$ requires N, 21·3 per cent.).

1:8-Carbazyl-5-aminobenzotriazole (IV).—The above nitro body was mixed with a little less than the theoretical quantity of stannous chloride and hydrochloric acid and heated under reflux for one hour.

On cooling, the double compound of the amine with stannic chloride separated out. This was collected, suspended in boiling water and decomposed by hydrogen sulphide. On cooling the precipitate consisting of the amine hydrochloride and stannic sulphide was filtered and extracted with boiling alcohol. The *amine* was precipitated from the extract by the addition of ammonia. Colourless plates (from xylene), m. p. 187-190°. (Found: C, 72·3 ; H, 4·6. $C_{18}H_{13}N_3$ requires C, 72·2 ; H, 4·3 per cent.).

The *acetyl* derivative of the amine was obtained by dissolving the compound in ethyl acetate and adding a slight excess of acetic anhydride. Rectangular plates, m. p. 292°. (Found: C, 70·4 ; H, 4·4; N, 20·5. $C_{20}H_{15}ON_3$ requires C, 70·1 ; H, 4·4 ; N, 20·5 per cent.).

Among the decomposition products of the compound during attempts at ring formation a small quantity of carbazole could be identified.

The Action of Nitrous Acid on 4:6-*Diamino*-1:3-*dianilinobenzene* (VI).—4:6-Dinitro-1:3-dianilinobenzene (Nietzki, and Schelder, *loc. cit.*) was however more easily reduced by treating the compound (35 g.) in alcohol with sodium hydrogen sulphide (from 164 g. of Na_2S, $9H_2O$) and boiling the mixture under reflux for 12 hours. The alcohol was then distilled over. The residue was diluted, the precipitate collected and washed successively with alcohol and benzene until it was obtained in colourless needles, m.p. 207° (yield 50 per cent.).

The diamine was suspended in acetic acid containing the requisite quantity of conc. HCl, and the calculated quantity of amyl nitrite was gradually added with vigorous stirring and cooling. A green mass separated which was collected after two hours. It was found impossible to crystallise it from any solvent. The same substance was formed when nitrous acid was allowed to act upon the diamine under varied conditions. An analysis of the body prepared by using pure substances showed that it contained chlorine.

However on attempting to recrystallise it from aniline a beautiful red compound was obtained which could then be recrystallised from xylene. Shining red plates, m. p. 253°. (Found: C, 82 ; H, 5·5 ; N, 12·6. $C_{30}H_{23}N_4$ requires C, 81·8 ; H, 5·4 ; N, 12·7 per cent.). It could not be acetylated or benzoylated. Its colour reaction with strong sulphuric acid was identical with that of azophenine and it was identified as such by converting it into flourindine. The green substance gave the corresponding derivative with toluidine. Red plates (from xylene), m. p. 264·5°. (Found:

C, 82·4 ; H, 6·4 ; N, 11·7. $C_{22}H_{16}N_4$ requires C, 82·5 ; H, 6·1 ; N, 11·9 per cent.). It would not condense with either mono-methyl or dimethyl anilines.

p-*Di-(o-nitranilino)-benzene.*—To a mixture of p-dibromobenzene (25 g.), o-nitraniline (30 g.) and finely powdered anhydrous potassium carbonate (80 g.), nitrobenzene (150 c.c.), a pinch of copper powder was added and the mixture heated at 200°, with efficient stirring for 6 hours when a deep red colour gradually developed. The solution was filtered hot when the condensation product crystallised. It was collected (80 g.) and washed with benzene, m. p. 228°. This crude product was treated with boiling alcohol to remove some 2-nitro-4'-bromodiphenylamine formed at the same time; yellowish red prisms from alcohol, m. p. 162°. (Found : N, 9·6. $C_{12}H_9O_2N_2Br$ requires N, 9·7 per cent.). A small portion of the *diainlino* compound was then recrystallised from nitrobenzene. Bright red prisms, m. p. 233°. (Found : N, 15·8. $C_{18}H_{14}O_4N_4$ requires N, 16 per cent.).

p-*Di-(o-aminoanilino)-benzene* (VII).—The reduction of the above dinitro compound is best accomplished in alcoholic suspension by means of sodium hydrogen sulphide. After refluxing for 12 hours the *diamine* separated in shining white plates (yield 90%), which, on recrystallisation from xylene as colourless rhombic plates, melted at 159°. (Found : N, 19·1. $C_{18}H_{18}N_4$ requires N, 19·3 per cent.).

p-*Phenylene-*1 : 1'-*dibenzotriazole* (VIII).—The finely powdered diamine (14·5 g.) was suspended in acetic acid (150 c.c.) containing conc. HCl (10 c.c.). The mixture was kept in ice well stirred. Sodium nitrite (7 g.) in conc. solution was gradully added, the temperature being maintained at 10°. After standing for two hours excess of water was added, the precipitate collected, dried and crystallised from nitrobenzene. Rectangular plates, m. p. 279°. (Found : N, 26·0. $C_{18}H_{12}N_6$ requires N, 26·0 per cent.).

It was not possible to identify any pure substance amongst the decomposition products of this compund during attempts at ring formation. Experiments were also tried to form only one triazole ring from the diamine, but without success. The unchanged diamine and the dibenzotriazole could be separated by extraction with xylene owing to the greater solubility of the former.

3-(2' : 4'-*Diaminoanilino*)-*carbazole.*—The compound (III) was reduced by means of the requisite quantity of stannous chloride and hydrochloric acid and the *amine* formed re-crystallised from xylene. Colourless rhombic plates, m. p. 256°. (Found : C, 79·8; H, 5·7; N, 15·2. $C_{18}H_{16}N_4$ requires C, 79·1; H, 5·5; N, 15·4 per cent.).

The analysis indicates that one of the nitro groups has been eliminated during the reduction. A small quantity of it in acetic acid was treated with nitrous acid. A clear solution was obtained which coupled readily with alkaline β-naphthol. Thus it is evident that the product is 3-(4-*aminoanilino*)-*carbazole*.

When however the dinitro body (III, 34 g.) was refluxed in alcohol (350 c.c.) with excess of sodium hydrogen sulphide (from 250 g. of $Na_2S, 9H_2O$), for 18 hours on a water-bath, the red colour formed at first disappeared entirely and the diamine separated out. This was collected and re-crystallised from xylene (yield 75 per cent.). Colourless rectangular prisms, m. p. 222°. (Found: C, 75·3; H, 5·8; N, 19·1. $C_{18}H_{16}N_4$ requires C, 75; H, 5·6; N, 19·4 per cent.).

On attempting to oxidise this substance with lead oxide (Fischer and Heiler, *loc. cit.*, and Fischer, *loc. cit.*), or with manganese dioxide in ammonical alcohol (Nietzki and Simon, *loc. cit.*) decomposition products were formed which could not be identified.

1-p-2′:4′-*Dinitroanilinophenylbenzotriazole*. — 1-*p*-Aminophenyl-benzotriazole (Ullmann, *Annalen*, 1904, **332**, 97) was condensed with 2:4-dinitrochlorobenzene by heating the two together in alcohol with sodium acetate under reflux for two hours. A red crystalline product separated. This was collected and recrystallised from xylene; yellowish red prisms, m.p. 228 . (Found: N, 22·3. $C_{18}H_{12}O_4N_6$ requires N, 22·3 per cent.).

1-p-2′:4′-*Diaminoanilinophenylbenzotriazole* (IX).—The above dinitro compound was reduced by means of stannous chloride and hydrochloric acid. On cooling and passing in HCl gas the stannic chloride double compound of the base separated out. This was collected and decomposed by H_2S. The *diamine* was carefully dried in a desiccator and recrystallised from toluene; colourless prisms, m.p. 155°-157°. (Found: C, 68·8; H, 5·2; N, 26·4. $C_{18}H_{16}N_6$ requires C, 68·3; H, 5·1; N, 26·6 per cent.).

2:7-*Diaminocarbazole*.—The diamine was prepared according to Tauber (*loc. cit.*) and obtained in colourless plates from xylene melting sharply at 260°. The *diacetyl* derivative was obtained in colourless shining plates melting with decomposition at 320°. (Found: C, 68·0; H, 5·3; N, 14·8. $C_{16}H_{15}O_2N_3$ requires C, 68·3; H, 5·3; N, 14·9 per cent.). The *dibenzylidene* compound formed pale yellow plates (from xylene), m.p. 290°. (Found: N, 11·4. $C_{26}H_{19}N_3$ requires N, 11·3 per cent.). With dimethylaminobenzaldehyde clusters of

yellowish red prisms (from xylene) m. p. 284° were obtained. (Found : N. 15·2. $C_{10}H_{8}N_{2}$ requires N, 15·2 per cent.).

Several experiments under varied conditions were tried in order to nitrate the diamino compound and its diacetyl derivative. High melting uncrystallisable products were obtained. An attempt was also made to replace the amino groups by hydroxyl groups through the diazo compound, and by treatment with excess of conc. sodium sulphite solution (compare Bucherer, *J. pr. Chem.*, 1904, **69**, 49). In the former case an uncrystallisable black solid was formed and in the latter the product was recovered unchanged even after boiling for two days under reflux.

Incidentally it was observed that 3-aminocarbazole was not affected by treatment with sodium sulphite.

Experiments on the Preparation of 3-Methylaminocarbazole.— Since it was found impossible to methylate 3-aminocarbazole directly by means of methyl iodide or dimethyl sulphate even under very vigorous conditions, the benzylidene compound (m. p. 214°, Mazzara and Leonardi, *Gazzetta*, 1891, **21**, II, 384) was prepared. But it was not possible to obtain addition compounds of this with methyl iodide or dimethyl-sulphate (compare Decker and Becker, *Annalen*, 1912, **395**, 362).

3-Aminocarbazole was condensed with p-toluenesulphonic chloride by heating the two together in molecular proportions in alcohol containing sodium acetate for 2 hours under reflux. On cooling and dilution, the *sulphonamide* separated out as a crystalline mass. It was then recrystallised from alcohol. Colourless plates, m. p. 227°. (Found : N, 8·3. $C_{19}H_{16}O_{2}N_{2}S$ requires N, 8·3 per cent.) It must be mentioned that in the above reaction the substance taken must be quite pure as otherwise a syrupy uncrystallisable solid is formed.

The sulphonamide was dissolved in a mixture of acetone and the calculated quantity of caustic soda (25 per cent.) and was methylated by the gradual addition of a slight excess of dimethyl sulphate while keeping the solution throughout alkaline and well stirred. It was allowed to stand for some time and on dilution the *methyl sulphonamide* separated as an oil which soon solidified. Colourless plates (from alcohol), m. p. 168°. (Found. N, 8. $C_{20}H_{18}O_{2}N_{2}S$ requires N, 8 per cent.).

Several experiments were made with the object of removing the sulphonyl groups by hydrolysis, but without success. Treatment with acids gave a green uncrystallisable low melting solid.

9-*Aminocarbazole* (X).—The amine (Wieland, Susser and Fressel,

loc. cit., m.p. 151°, yield 20 per cent.) was dissolved in alcohol to which a slight excess of *cyclo*hexanone had been added and the mixture allowed to stand for 12 hours, after which it was gently refluxed on a water-bath for two hours. On cooling the *hydrazone* separated out in clusters of large well defined rectangular prisms, m. p. 96°. (Found : N, 10·4. $C_{18}H_{18}N_2$ requires N, 10·7 per cent.).

Several experiments were made in order to remove ammonia from the above compound by heating it with various acids to obtain an indole ring. Sticky uncrystallisable solids were formed which could not be purified.

9-*Nitrosohexahydrocarbazole* (XII).—Hexahydrocarbazole was prepared according to Perkin, jun., and Plant (*J. Chem. Soc.* 1924, **125**, 1512) by the electrolytic reduction of tetrahydrocarbazole. It was found that 20 gm. of tetrahydrocarbazole dissolved in 200 c. c. of strong sulphuric acid (*d* 1·5) were completely reduced by a current of 6 amperes during 16 hours ; m. p. 99°.

This was converted to the nitroso derivative by treating its acetic acid solution with sodium nitrite. On diluting the reaction mixture a thick oil separated out which soon solidified to a yellow mass. Large brown prisms from alcohol, m. p. 61-62°. (Found : N, 13· 9. $C_{12}H_{14}ON_2$ requires N, 14·0 per cent. Compare Borsche, Witte and Bothe, *loc. cit.*, p. 70).

An experiment to obtain 9-*aminohexahydrocarbazole* in the same manner as 9-aminocarbazole resulted in a sticky product consisting mainly of hexahydrocarbazole itself.

8 : 9-(1 : 2-*cycloHexyl*)-*tetrahydrocarbazole*   (XIII).—9-Nitrosohexahydrocarbazole (10 g.) was dissolved in acetic acid (100 c. c.) containing a slight excess of *cyclo*hexanone (7· 5 c. c.). Zinc dust (80 g.) was gradually added during 1 hour while vigorous stirring was maintained and the temperature kept as low as possible by ice cooling. The excess of zinc dust was removed and the clear solution allowed to remain overnight. It was then heated on a water-bath for 1 hour, when on cooling and dilution with water a thick gum separated out. This was washed with water and dissolved in ether. The ether solution was repeatedly washed successively with water, dilute hydrochloric acid, and sodium carbonate solution, finally it was shaken up with animal charcoal, filtered and dried. On removing the ether a thick syrupy solid remained which was distilled under reduced pressure. The clear distillate between 230° and 240°/18 mm. solidified on scratching with a drop of methyl alcohol. It was recrystallised from alcohol (yield 8 g.). Colourless prisms, m. p.

88°. (Found : C, 85·9 ; H, 8· 4 ; N, 5· 6. $C_{18}H_{21}N$ requires C, 86· 0 H, 8·4 ; N, 5· 6 per cent.).

This compound was insoluble in dilute acids ; in dry ether it did not give a *hydrochloride* when hydrochloric acid gas was passed in. The *picrate* was obtained by heating molecular proportions of the substance and picric acid in alcohol for a few minutes. It crystallised out on cooling in bright yellow prisms melting with decomposition at 138°. On heating the substance in a sealed tube with excess of methyl iodide for 12 hours at 100°, and evaporating off the excess of methyl iodide, a compound (colourless prisms) was obtained which was insoluble in ether, contained iodine and melted between 50° and 70° with decomposition. It was not possible to purify it.

Experiments were made to dehydrogenate the above compound. But it was necessary to ascertain first what would happen to hexahydrocarbazole under conditions when tetrahydrocarbazole gave carbazole. It was found that when the vapours of hexahydrocarbazole were passed over heated lead monoxide pure carbazole was formed (Borsche, Witte and Bothe, *loc. cit.*). Sulphur reduction (Perkin, jun., and Plant, *loc. cit.*) also gave carbazole (2 g. from 10 g.).

When however 8 : 9- (1′ : 2′ -*cyclo*hexyl)- tetrahydrocarbazole was heated with lead monoxide, a tar distilled over. When reduced by sulphur it was not possible to isolate any pure compound.

8 : 9-(1 : 2′-*cycloHexyyl*)-*tetrahydrocarbazole.*—The compound (XIII 5 g.) was dissolved in sulphuric acid (150 c. c., d 1· 5), and the solution was reduced in the cathode chamber by a current of 6 ampere for 16 hours. On dilution and making alkaline with ammonia a sticky white solid separated out. As this could not be recrystallised from any solvent it was distilled under reduced pressure. The fraction boiling at 235°-245°/15 mm. solidified and was recrystallised from alcohol. Colourless glistening plates, m. p. 144°. (Found : C, 65·8 ; H, 9·0 ; N, 5·2. $C_{18}H_{23}N$ requires C, 65·4 ; H,9·1 ; N, 5·5 per cent.).

This compound was markedly basic dissolving in dilute acids. A crystalline *hydrochloride* (m. p. 225° decomp.) was obtained from its ethereal solution. The *picrate* separated from alcohol in yellow prisms melting at 160°. The *methiodide* was prepared by heating it with excess of methyl iodide in a sealed tube at 100° for 12 hours. On cooling it crystallised in colourless prisms melting with decomposition at 187°.

An attempt was made to dehydrogenate this compound by passing its vapour over heated lead monoxide. The product obtained contained some tar. But on recrystallisation from glacial acetic acid a small quantity (0·2 g. from 10 g.) of a crystalline compound (colourless plates) was obtained. This melted at 140° and depressed the melting point of the original compound." But it was not possible to examine it further.

6-*Methylhexahydrocarbazole*.—6-Methyltetrahydrocarbazole was prepared according to Borsche, Witte and Bothe (*loc. cit.*, p. 62 ; m. p. 148°).

It was then reduced electrolytically in the same manner a tetrahydrocarbazole. It was noticed that if perfectly pure 6-methyltetrahydrocarbazole was used there was no sign of reduction, but its was not possible to determine the nature of the catalyst. 6-*Methylhexahydrocarbazole* separated out as an oil which slowly solidified. As it was not possible to crystallise it owing to its tendency to separate out as an oil, a portion of it was distilled under reduced pressure. The distillate, b. p. 230-240°/14 mm. on solidifying consisted of colourless prisms, m. p. 43-44°. (Found : C, 83· 7 ; H, 9.2 ; N, 7·4. $C_{13}H_{17}N$ requires C, 83·4 ; H, 9·1 ; N, 7·5 per cent.).

The picrate was prepared in the usual manner and was found to melt with decomposition at 174°. The *nitroso derivative* consisted of brownish yellow prisms (from alcohol), m. p. 71°. (Found : N, 13· 0. $C_{13}H_{16}ON_2$ requires N, 13·1 per cent.).

6-*Methyl-8:9-(1' : 2'-cyclohexyl)-tetrahydrocarbazole* - 6-Methyl-9-nitrosohexahydrocarbazole dissolved in acetic acid containing a slight excess of *cyclo*hexanone and was reduced by means of zinc dust in the manner described under the preparation of compound (XIII). The product was distilled under reduced pressure. The fraction, b. p. 240°-250°/18 mm., consisted of a thick syrup (2 g. from 10 g. of the nitroso-compound) that did not solidify even after long keeping. An analysis of it showed that nitrogen was 1% too low. The *picrate* was prepared and recrystallised from alcohol, pale yellow prisms decomposing at 118°. (Found : C, 60·8 ; H, 5·3 ; N, 11. $C_{25}H_{28}O_7N_4$ requires C, 60·7 ; H, 5·3 ; N, 11·8 per cent.).

I desire to express my gratitude to Prof. W. H. Perkin. jun., for his continued help and interest throughout this work. My thanks are due to Mr. F. Hall for the analyses.

Halogenation. Part III. Bromination.

By Phuldeo Sahay Varma and Badri Narayan.

Bromination of aromatic hydrocarbons has been effected directly in presence as well as in absence of halogen carriers. Bromobenzene has been obtained from boiling benzene and bromine vapour by Couper (*Annalen*, 1857, **104**, 225). Brunner has effected the bromination of benzene by one molecule of bromine at the room temperature in 150 days up to 94 per cent. (*Chem. Zentr.*, 1900, II, 251). Bromination has also been brought about in the presence of 1—2 per cent. of iodine (Schramm. *Ber.*, 1885, **18**, 515 ; Michaelis and Groff, *Ber.*, 1875, **8**, 926), in the presence of aluminium-mercury couple (Cohen and Dakin, *J. Chem. Soc.*, 1899, **76**, 894), in the presence of zinc chloride (Schiaparelli, *Gazzetta*, 1881, **11**, 70), in the presence of aluminium chloride (Green, *Compt. rend.*, 1880, **90**, 41) and in the presence of pyridine (Cross and Cohen, *Proc. Chem. Soc.*, 1908).

Gattermann ("Die Praxis des Organishen Chemikers") obtained bromo-benzene in the presence of iron filings. A few cases of bromination with aqueous hypobromous acid (Stark. *Ber.*, 1913, **46**, 670) have also been effected. Datta and Chatterjee (*J. Amer. Chem. Soc.*, 1916, **38**, 2545) introduced bromine in the aromatic hydrocarbons by means of bromine and concentrated nitric acid, but the yield of the bromo-compound, by this method, has not been found to be satisfactory by the authors.

Attempts have been made by the authors in this investigation to bring about bromination in presence of (*i*) a mixture of nitro-sulphonic acid and fuming nitric acid, (*ii*) concentrated or fuming sulphuric acid, (*iii*) concentrated or fuming nitric acid, (*iv*) a mixture of concentrated or fuming sulphuric acid and concentrated or fuming nitric acid, and (*v*) sodium nitrite and concentrated or fuming sulphuric acid.

The results obtained by using a mixture of nitro-sulphonic acid and fuming nitric acid are summarised in Table. I. It has been found possible by this method to get 10·8 g. of bromobenzene from 10 c.c. of benzene and 8 c.c. of bromine, a yield which has not been obtained by any method known up till now when the amount of bromine used in the experiment is taken into consideration.

In the methods of Cross and Cohen (*loc. cit.*) and of Gattermann (*loc. cit.*) which are generally used in the laboratory for preparing bromobenzene, a much larger quantity (8 c.c.) of bromine is used to obtain about 12 g. of bromobenzene from 10 g. of benzene.

It is interesting to find that while the presence of a small quantity of acetic acid in iodination is capable of increasing the yield of iodo-compounds to a considerable extent (Varma and Kulkarni, this *Journal*, 1926, 3, 291 ; Varma and Panickar, *ibid*, 1926, 3, 342), the presence of acetic acid has no appreciable effect in the case of bromination.

. In addition to bromobenzene, it has been possible in the presence of this mixture of nitro-sulphonic acid and fuming nitric acid to get a good yield of *p*-dibromobenzene from benzene itself or from bromobenzene, *p*-bromo-iodobenzene from iodobenzene, *o*- and *p*-bromo-toluene and penta-brom-benzoic acid from toluene, bromo-xylenes from *p*-xylene. *o*-Chlorotoluene and *p*-iodotoluene are oxidised to chlorobenzoic and iodobenzoic acids respectively.

Bromination has also been effected in presence of sulphuric acid. The results obtained are summarised in Table II. Concentrated sulphuric acid gives but a poor yield of the bromo-derivative whilst fuming sulphuric acid containing 10 per cent. of sulphur trioxide gives as much as 8·8 g. of bromobenzene from 10 c.c. of benzene and 5 c.c. of bromine. This yield is lower than that obtained by using the nitro-sulphonic acid mixture. The formation of the sulphonic acid derivative as the intermediate product during the course of the reaction does not seem probable as benzene sulphonic acid itself is not affected at all by bromine (*vide* Table II, Expt. 13).

Nitric acid is also capable of bringing about bromination. The results are summarised in Table III. The yield of the bromo-derivative is very poor when concentrated nitric acid alone is used but fuming nitric acid (*d* 1·52) gives a better yield, nearly the same that is obtained by using fuming sulphuric acid. A mixture of fuming sulphuric acid and fuming nitric acid (equal volumes of each) is equally effective though not better than any one of them.

The presence of sodium nitrite and sulphuric acid also brings about bromination but the yield is far short of that obtained by using the nitro-sulphonic acid mixture. The results are summarised in Table IV. In this case the use of fuming sulphuric acid does not seem to have any clear advantage over that of ordinary concentrated sulphuric acid.

EXPERIMENTAL.

Bromination in presence of fuming nitric and nitro-sulphonic acid mixture.

The above mixture is prepared by passing a steady current of dry sulphur dioxide into cold fuming nitric acid (*d* 1·52) until about 50 per cent. of nitro-sulphonic acid is obtained. If the percentage of nitro-sulphonic acid in the mixture is greater than 50 per cent., it is brought down to this value by adding to it the required quantity of fuming nitric acid. A mixture thus prepared is used in the following experiments.

In the experiments tabulated below, benzene and bromine are taken in a round-bottomed flask and heated on a water-bath under reflux condenser. The nitro-sulphonic acid mixture is then added from the upper end of the condenser tube, one c.c. at a time, at intervals of ten minutes. When the whole of the mixture is added the contents of the flask are heated for a further period mentioned against the experiments, and in some cases, left to stand for some hours or overnight. The reacting mixture is then washed twice with distilled water in a separating funnel and subsequently with a very dilute caustic soda solution. It is finally again washed with distilled water and then dehydrated with fused calcium chloride and distilled. The fraction distilling between 150° and 170° is first collected. This fraction is re-distilled and the portion now distilling at 155°-165° is collected separately and found to be mono-bromo-benzene. The residue, if any, left in the distilling flask is crystallised from rectified spirit and identified.

It is clear from the above table that any attempt to get a better yield of mono-bromobenzene by increasing the period of heating on the water-bath or by increasing the quantity of the nitro-sulphonic acid mixture or of bromine results in the decrease of the yield.

Bromination in presence of concentrated or fuming sulphuric acid.—The procedure adopted in this case is exactly the same as that mentioned in the preceding one. Here only concentrated sulphuric acid (*d* 1·84) or fuming sulphuric acid containing 10 per cent. of SO_3 is used in place of the nitro-sulphonic acid mixture used in the preceding case. The results obtained are summarised in Table II.

TABLE I.

Expt.	Benzene (in c.c.)	Bromine (in c.c.)	Acetic acid.	Nitro-sulphonic mixture (in c.c.)	Time allowed for reaction (in hrs)	Monobromo-derivative (in gm.)	Di- or poly-bromo or other derivatives.
1	10	3	...	6	3	8·6	Very little residue left.
2	,,	,,	3 c.c.	·,	,,	8·9	,, ,,
3	,,	,,	4 ,,	,,	,,	8·5	,, ,,
4	,,	,,	...	10	,,	10·2	,, ,,
5	,,	,,	...	,,	4	10·8	,, ,,
6	,,	,,	...	13	,,	9·1	Some residue left.
7	,,	,,	2 c.c.	10	3	8·8	0·9g. of 1:3 :5-tri-bromoben-zene.
8	,,	6	...	10	,,	9·0	2·1 g. of p-di-bromobenzene.
9	,,	3	...	10	4*	very little	3·8 g. of p-di-bromobenzene.
10	,,	6	...	,,	4*	,,	6·0 g. of p-di-bromobenzene.
11	Chloroben-zene 5 g.	1·4	...	,,	4*	Bromo-chlo-robenzene (3·5 g.).	
12	Bromoben-zene (10 c.c.)	2·4	...	,,	4*	p-Dibromo-benzene (6·2 g.).	
13	Iodobenzene (3·5 c.c.)	0·9	...	,,	5(days)	p-Bromo-iodo-benzene (2·6 g.).	
14	,, 10 c.c.	2·3	...	10	4	p-Bromo-iodo-benzene (10 g.).	
15	Nitrobenzene (10 c.c.)	2·5	...	,,	4†	No change.	
16	Toluene (10 c.c.)	2·5	...	,,	4*	o- and p-Bro-motoluene (5·5 g.).	1·8 g. of penta-bromobenzoic acid.
17	p-Xylene	2·2	...	,,	4*	5-Bromo-xy-lene (3·2 g.)	4-Bromo-xy-lene ; ω-bro-moxylene (1·5 g.). Tetrabromo-xylene (1·9 g.).
18	o-Chloroto-luene (5 c.c.)	1·1	...	5	4*	No bromo derivative.	Chlorobenzoic acid (2·6 g.).
19	p-Iodo-tolu-ene (10 c.c.)	2·0	...	10	4*	No bromo derivative.	Iodo-benzoic acid (4·4 g).

* Allowed to stand for two hours more.

† Allowed to stand overnight.

TABLE II.

Expt.	Benzene (in c. c.)	Bromine (in c. c.)	Acetic acid.	Conc. H_2SO_4	Fuming H_2SO_4	Time allowed for reaction (in hrs.)	Monobromo-derivative (in gm.)	Poly-bromo-derivative.
1	10	3	...	10 c.c.	...	4	3·2	...
2	,,	6	...	10 c.c.	...	4	3·8	3·2 g. of p-di-bromoben-zene.
3	,,	8	...	...	20 c.c.	4	4·3	0·9 g. of p-di-bromoben-zene.
4	,,	4	...	...	10 ,,	2	6·1	...
5	,,	4	...	...	15 ,,	2	7·0	...
6	,,	5	...	...	10 ,,	2	7·4	A little of di-bromoben-zene.
7	,,	6	...	...	10 ,,	2	8·8	0·8 g. of dibro-mobenzene.
8	,,	6	8 c.c.	...	10 ,,	2	7·2	0·6 g. of dibro-mobenzene.
9	,,	6	...	...	15 ,,	2	8·5	0·6 g. of dibro-mobenzene.
10	,,	6	3 c.c.	...	15 ,,	2	7·9	0·8 g. of dibro-mobenzene.
11	,,	6	...	...	20 ,,	4	little	5·5 g. of dibro-mobenzene.
12	Benzene sulphonic acid 5 g.	3	...	...	...	4	no bromina-tion.	...
13	Toluene 10 c. c.	2·5	...	...	10 ,,	2	5·0	...
14	Toluene 10 c. c.	3·5	...	...	10 ,,	2	6·8	...
15	Xylene 10 c. c.	2·5	...	...	7 ,,	2	bromo-deri-vative mainly 5-bromo-xy-lene (5·3).	...

Bromination in presence of concentrated or fuming nitric acid or a mixture of nitric and sulphuric acid.

The procedure adopted in this case is the same as that described in the preceding ones. The results obtained are summarised below. Concentrated nitric acid used in these experiments has the sp. gr. 1·44 while fumming nitric acid has the sp. gr. 1·52. Fuming sulphuric acid contains about 10 per cent. of sulphur trioxide.

TABLE III.

Expt.	Benzene (in c.c.)	Bromine (in c.c.)	Conc. HNO₃ (in c.c.)	Fuming HNO₃ (in c.c.)	Conc. H₂SO₄	Fuming H₂SO₄.	Time allowed for reaction (in hrs.)	Mono-bromo-derivative (in gms.)
1	10	3	10	...	...	...	4	1·9
2	,,	,,	...	10	...	...	..	8·6
3	,,	,,	...	5	...	5 c.c.	,,	8·8
4	,,	,,	...	8	...	2 c.c.	,.	7·2
5	,,	,,	...	5	5 c.c.	...	.,	6·2

4. *Bromination in presence of sodium nitrite and concentrated or fuming sulphuric acid.*

The experiments have been carried out in this case by taking benzene, bromine and sodium nitrite in a round-bottomed flask which is heated on a water-bath. When the benzene begins to boil, sulphuric acid is added from the upper end of the condenser one c.c. at a time at interval of ten minutes. The flask is vigorously shaken from time to time, when the whole of the acid is added, the reacting mixture is further allowed to be heated on the water-bath till 4 hours are completed. The resulting product is first washed with water, then with dilute caustic soda solution and finally again with water. It is dehydrated with fused calcium chloride and distilled as before. The results obtained are summarised below.

TABLE IV.

Expt.	Benzene (in c.c.)	Bromine (in c.c.)	Sodium nitrite (in gms.)	Conc. H_2SO_4 (in c.c.)	Fuming H_2SO_4.	Time allowed for the reaction (in hrs.)	Mono-bromo-benzene (in gms.)
1	10	3	5	10	...	4	5
2	,,	3	15	20	...	,,	5·4
3	,,	5	15	20	...	,,	6·2
4	,,	4	15	20	...	,,	5·7
5	,,	4	20	20	...	,,	4·8
6	,,	3	12	20	..	,,	5·8
7	,,	3	5	..	10 c.c.	,,	5·8
8	,,	3	15	...	15 c.c.	,,	5·3
9	,,	3	10	...	20 c.c.	,,	6·2

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The Action of Carbon Tetrachloride on Certain Mercaptans.

By Sri Krishna and Sajjan Singh.

Reimer and Tiemann (*Ber.*, 1876, **9**, 1285; 1877, **10**, 824) investigated the action of carbon tetrachloride on phenols in alkaline solution, and they found that carbon tetrachloride is but slowly acted upon when heated with an aqueous solution of phenol in excess of alkali, but in alcoholic solution the reaction proceeds more rapidly, the products being *ortho*-and *para*-hydroxybenzoic acids. The products, however, are quite different when the conditions of the experiment are slightly altered, for instance, the production of aurine and rosolic acid from phenol and salicylaldehyde which is an intermediate product, under the dehydrating influence of the excess of alkali (*Ber.* 1877, **10**, 824). It, therefore, seems that the action of carbon tetrachloride and chloroform on phenols does not always proceed as has been shown by Reimer and Tiemann. Employing zinc chloride as a condensing agent Sen, Sinha and Sarkar (*J. Indian Chem. Soc.*, 1925, **1**, 303) have obtained benzeins from phenols and chloroform.

An attempt has now been made to study the products that result from mercaptans when heated with carbon tetrachloride and alkalis according to the above method. As a result of this investigation it is found that unsubstituted thiophenol gives thiosalicylic acid together with a large quantity of its disulphide. Substituted thiophenols, on the other hand, produce an acid from their disulphides.

$$C_6H_5.SH + CCl_4 + 6KOH = C_6H_4 {< \atop {SK \atop COOK}} + 4KCl + 4H_2O$$

$$2\,(R{\cdot}C_6H_4SH) \xrightarrow{O} (R{\cdot}C_6H_4{\cdot}S{\text-}S{\cdot}C_6H_4{\cdot}R)$$

$$(R{\cdot}C_6H_4{\cdot}S)_2 + CCl_4 + 5KOH = R{\cdot}C_6H_4{\cdot}S{\text-}S{\cdot}C_6H_4{\cdot}R{\cdot}COOK + 4KCl + 3H_2O.$$
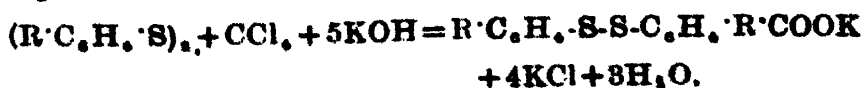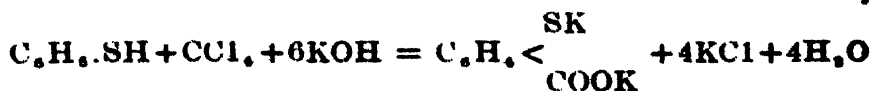
This shows that the action of alkali firstly is to convert the mercaptan into a disulphide. This, however, is not in accordance with the previous experiments where the disulphide is broken up by the alkalis to form mercaptans (Schiller and Otto, *Ber.*, 1876, **9**, 1687; Smiles and Steward, *J. Chem. Soc.*, 1921, **119**, 1794):

$$HCO_2 \cdot C_6H_4 \cdot S\text{-}S \cdot C_6H_4 \cdot CO_2H + H_2O = HO_2C \cdot C_6H_4 \cdot SH$$
$$+ OH \cdot S \cdot C_6H_4 \cdot CO_2H$$
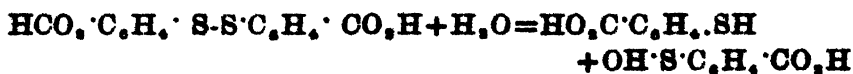
The formation of the thiol derivatives from the disulphide indicates that rupture of the dithio-system has taken place, and since it cannot be supposed that under these conditions the change is due to direct reduction by any reagent present, it must be assumed that the process is primarily one of hydrolysis which is effected by the alkali hydroxide. In the present case, high temperature and pressure at which the experiment is performed are probably responsible for the production of the disulphide.

The view that an acid from the disulphide is one of the products, is found to be correct, as it can be very easily reduced to the corresponding mercaptan and the acid from the mercaptan:

$$R \cdot C_6H_4 \cdot S\text{-}S \cdot C_6H_4 R \cdot COOH \longrightarrow R \cdot C_6H_4 \cdot SH$$
$$+ COOH \cdot R \cdot C_6H_4 \cdot SH.$$
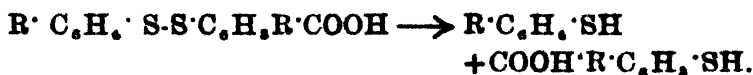
Possibilities of the reaction taking a different course from what is shown above are many, e.g.,
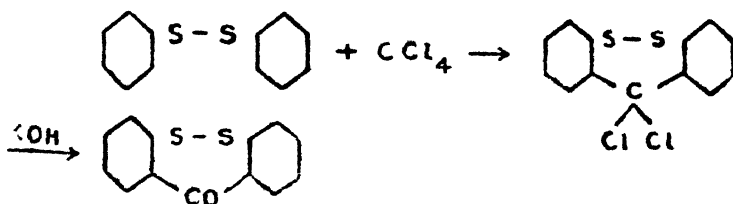
Such is not the case is borne out by the experimental results, unless we assume that on reduction the hydrolysis of the carbonyl group takes place:
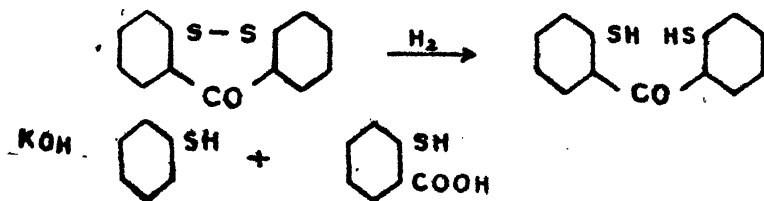
The yield of the products obtained is very small and in none of the experiments has it been more than 12 per cent. It makes no difference in the yields of the final products, whether sodium or potassium hydroxide is employed. This is brought out because Reimer and Tiemann (*loc. cit.*) insist on using potassium hydroxide for obtaining good results, especially in presence of small amounts of alcohol. The results obtained in the present work show that the presence of alcohol in howsoever small a quantity is detrimental to the success of the experiment.

Efforts have been made to improve the yield of the products by employing suitable catalysts. Shah (*J. Indian Inst. Sci.*, 1924, 20) has successfully employed reduced copper in similar condensations of aniline and carbon tetrachloride, but in these experiments it is found that reduced copper and reduced nickel inhibit the reaction.

The effect of temperature and the length of heating have also been noticed as shown in the following tables :—

Temperature.	Hrs. of heating.	Percentage of thiol acid.	Other products.
100-110°	24	12	Small quantity of silica and the rest unchanged together with resinous products.
120-130°	24	4	
130-140°	24	3	Resinous products.
150-160°	24	nil	

Length of heating at 100-110°.

Hrs. of heating.	Percentage of the acid formed.
6	2
8	4
16	6
24	12
32	8
40	5
48	3

On longer heating various resinous, noncrystallisable products were formed.

The usual method of preparing thiophenol from benzenesulphonic acid and phosphorous pentachloride and the reduction of the resulting sulphonyl chloride is found to be lengthy and tedious ; it was, therefore, prepared directly from benzene and chlorsulphonic acid. The details of the method are given below.

EXPERIMENTAL.

Thiophenol, $C_6H_5.SH$.—Into a flask containing chlorsulphonic acid (600 g., 5 mols.) cooled to $0°$ was added drop by drop from a separating funnel pure dry benzene (80 g.) in the course of an hour. As soon as a drop came in contact with chlorsulphonic acid, hydrogen chloride was evolved and the temperature rose. In order to avoid any undue rise in temperature, the mixture was thoroughly stirred. When whole of the benzene had been added, the mixture was warmed on a water-bath for an hour at 65-70°. The mixture was cooled and poured over crushed ice, when benzene sulphonyl chloride separated out as a white solid (yield 80 per cent.). The acid water was drained off and more ice added. The process was repeated thrice when most of the acid was got rid off. It is difficult to filter the sulphonyl chloride on a water-pump, as it melts at a low temperature.

The sulphonyl chloride (20 g.) thus obtained was then added in small portions to cooled (0°) 50 per cent. sulphuric acid (80 c.c.) and the calculated quantity of zinc dust (40 g.) was added to the mixture without letting the temperature rise. The flask was then fitted with a reflux condenser and shaken for half an hour, any rise in temperature being avoided. The mixture was then heated on a small flame for five hours and then steam distilled when theophenol came over as a pale yellow liquid.

o-Thiolbenzoic Acid.—A mixture of potassium hydroxide (36 g.) disolved in a small quantity of water, thiophenol (12 g.) and carbon tetrachloride (17 g.) were sealed in a thick glass tube and heated in a furnace at 100-110° for 24 hours. The contents of the tube (yellow liquid and brownish red solid) were washed into a beaker and excess of carbon tetrachloride removed on a water-bath. On cooling the mixture was extracted with ether to remove unacted thiphenol and disulphide, and the aqueous layer, after filtration, was rendered acidic when a yellow precipitate settled down. It

crystallised from alcohol as white needles, m.p. 177°. The analysis agreed with the formula for o-thiolbenzoic acid. (Literature gives the m.p. 165° for o-thiolbenzoic acid). The potassium salt was prepared and the analysis again showed this to be that of thiolbenzoic acid.

4 : 4′-Dichloro-6′(?)-carboxyl diphenyl disulphide (SH : Cl : COOH = 1 : 4 : 6′) was obtained by heating molecular proportions of p-chlorothiophenol and carbon tetrachloride in a sealed tube for 24 hours at 110°. The contents of the tube, on removal of CCl_4 and resinous matter, were acidified and the white precipitate thus formed was collected and crystallised; m.p. 210-12°. (Found : S, 19·67; Cl, 21·42. $C_{13}H_8O_2Cl_2S_2$ requires S, 19·33; Cl, 21·45 per cent).

Thiol-4-chloro-2 (?)-benzoic acid (SH : Cl : COOH = 1 : 4 : 2) was obtained from the above disulphide on reduction with zinc and hydrochloric acid in alcoholic solution. On pouring the mixture in water an oil and a solid separated. The oil, on keeping, solidified and was identified as p-chlorothiophenol, and the solid, on crystallisation from alcohol, gave colourless needles, m.p. 110°. (Found : S, 17·65; Cl, 18·50; C, 44·04; H, 2·83. $C_7H_5O_2SCl$ requires S, 16·97; Cl, 18·83; C, 44·56; H, 2·64 per cent.).

2 : 2′ : 5 : 5′ Tetrachloro-6′ (?)-carboxyl diphenyl disulphide.— This was prepared from 1 : 4-dichlorothiophenol and carbon tetrachloride. It crystallised from acetic acid in plates, m.p. 176°. (Found : S, 16·29; Cl, 35·22. $C_{13}H_6O_2S_2Cl_4$ requires Cl, 35·50; S, 16·00 per cent.).

Thiol-2 : 5-dichloro-6 (?)-benzoic acid (SH : Cl : Cl : COOH = 1 : 2 : 5 : 6) was formed when the above disulphide was carefully reduced in acetic acid solution with zinc dust. On dilution with water, the products were separated on treatment with sodium carbonate. The acid obtained on neutralisation with mineral acids was crystallised from alcohol in needles, m. p. 122° (D.R.P. 234375 gives no melting point.) (Found : C, 37·55; H, 3·10; Cl, 31·44; S, 14·60. $C_7H_4O_2Cl_2S$ requires C, 37·66; H, 1·79; Cl, 31·83; S, 14·35 per cent.).

4 : 4′-Dimethyl-8′ (?)-carboxyl diphenyl disulphide was obtained from p-tolyl mercaptan and carbon tetrachloride. It was crystallised from acetic acid in needles, m.p. 156°. (Found : S, 21·71. $C_{15}H_{14}O_2S_2$ requires S, 22·06 per cent.).

Thiol-4-methyl-3 (?)-benzoic acid (SH : CH_3 : COOH = 1 : 4 : 3) was obtained from the above disulphide on reduction in acetic acid solution. It crystallises in needles, m.p. 82° (D. R. P. 216269

gives no melting point). (Found: C, 56·71; H, 5·01; S, 18·90. $C_3H_5O_4S$ requires C, 57·14; H, 4·76; S, 19·04 per cent.).

4:4'-*Diamino-3'(?)-carboxyl diphenyl disulphide hydrochloride* was prepared from p-nitrothiophenol and CCl_4. It crystallises from alcohol in colourless plates and chars at 280°. (Found: Cl, 19·21; S, 17·73. $C_{13}H_{14}O_2Cl_2N_2S$ requires S, 17·58; Cl, 19·45 per cent.).

Thiol-4-amino-3 (?)-benzoic acid hydrochloride ($SH:NH_2:COOH$ $=1:4:3$) was prepared from the above disulphide on reduction with zinc and hydrochloric acid. (Found: C, 40·38; H, 4·21; N, 6·60. $C_7H_8O_2NSCl$ requires C, 40·87; H, 3·89; N, 6·81 per cent.).

·4:4'-*Dibromo-6'(?)-carboxyl diphenyl disulphide* was prepared from p-bromothiophenol and carbon tetrachloride. It crystallises from acetic acid in needles, m. p. 241-42°. (Found: Br, 37·83; S, 15·69. $C_{13}H_8O_2S_2Br_2$ requires Br, 38·09, S, 15·20 per cent.).

On reduction in acetic acid solution with zinc dust it gives p-bromothiophenol and *thiol-4-bromo-3(?)-benzoic acid* ($SH:Br:COOH=$, $1:4:3$), which crystallises from alcohol in silky needles, m.p. 210°. (Found: C, 35·65; H, 3·11; S, 14·01; Br, 33·93. $C_7H_5O_2SBr$ requires C, 36·05; H, 2·14 ; S, 13·73; Br, 34·33 per cent.).

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A Note on a Comparative Study of the Preparation of Anthraquinone.

By Phuldeo Sahay Varma and Jyotsna Lal Das Gupta.

Attempts have been made by the authors to make a comparative study of the various methods described in literature for the oxidation of anthracene to anthraquinone. So far Fischer's chromic acid method has been found to be the best in giving the maximum yield but the process involves the use of materials which are comparatively costly. A cheaper and fairly satisfactory method of oxidising anthracene has been devised by using oxides of nitrogen. The yield of anthraquinone obtained by different methods is summarised below :

	Reagents.	Yield of sublimed anthraquinone from 5 g. of pure anthracene.
1.	Chromium trioxide and glacial acetic acid (Graebe and Liebermann's method) ...	3·6 g.
2.	Chromium trioxide and glacial acetic acid (as modified by Fischer)	4·3 ,,
3.	Sodium dichromate and sulphuric acid ...	3·0 ,,
4.	Sodium nitrate and magnesium chloride ...	2·8 ,,
5.	Nitric acid and glacial acetic acid ...	3·0 ,,
6.	Dilute nitric acid	2·3 ,,
7.	Sodium nitrate and sulphuric acid ...	3·2 ,,
8.	Sodium nitrate and acetic acid	2·4 ,,
9.	Oxides of nitrogen in presence of water or rectified spirit	3·0 ,,
10.	Oxides of nitrogen in presence of sulphuric acid, dilute or strong	2·5 ,,
11.	Oxides of nitrogen in presence of acetic acid or chloroform· or carbon tetrachloride or benzene or nitrobenzene	1·5 to 2·5 g·

In the case of the oxides of nitrogen the procedure adopted has been as follows :—

The oxides of nitrogen obtained by warming arsenious oxide and strong nitric acid are passed in anthracene (5 g.) suspended in water (25 c.c.) or rectified spirit (25 c.c.) or other solvents mentioned above. There is no apparent change for the first few minutes. The temperature then begins to rise gradually and remains stationary between 60° and 70° for some time. Meanwhile the substance turns yellowish. The absorption of the gas is not so rapid in the case of water as some of it escapes unabsorbed but it is comparatively rapid in the case of rectified spirit and other solvents. The mixture is shaken from time to time. When no more gases are seen to be absorbed, the reacting mixture is removed and warmed on water-bath for about an hour. Considerable evolution of the oxides of nitrogen takes place during this time. The solid residue left is separated, pressed between filter papers, dried and sublimed.

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Zinc Oxide as a general Sensitiser for Photochemical Reactions.

By A. K. Bhattacharya and N. R. Dhar.

If a system is not sensitive to light, it suffices at times to add to it a small quantity of another substance in order to make it sensitive to the action of rays absorbed by that substance. This action is known as *photochemical sensitisation* and the substance, which absorbs the light and provokes the reaction without apparently taking part in it, is called a *sensitiser*.

There is a class of photo-sensitisation in which a system which is chemically influenced by certain radiations is rendered sensitive to rays of another wave-length by a substance which absorbs these rays. Several years ago (Weigert, *Zeit. physikal. Chem.*, 1912, **80**, 103) showed that ozone, which is decomposed by ultraviolet rays but not much by visible light is decomposed readily under the action of blue light when mixed with chlorine. Similarly in a foregoing paper (*Zeit. anorg. Chem.*, 1923, **128**, 212), we have shown that the decomposition of Fehlings' solution, cupri-ammonium oxalate, Eder's mixture [$HgCl_2$ and $(NH_4)_2C_2O_4$], a mixture of mercuric chloride and a tartrate etc., can be markedly accelerated by ferric or uranyl salts under the influence of sunlight. Moreover, eosin, chlorophyll and several other substances have been used as sensitisers.

In a foregoing paper (*Zeit. physikal. Chem.*, 1926, **120**, 302), we have explained photo-sensitisation from the point of view of the activation of molecules from the Franck-Cario point of view. For example, in the sensitisation of the decomposition of ozone in presence of chlorine, we can assume that by the absorption of blue light, the chlorine molecules get activated and such chlorine molecules are instrumental in bringing about the decomposition of ozone or· the photochemical combination of hydrogen and oxygen in sunlight as observed by Norrish. Similarly, by the absorption of visible light, a molecule of chlorophyll is activated and this active molecule induces the chemical change between carbon dioxide and water vapour in plants.

In this investigation we have carried on numerous experiments with several photochemical reactions in presence of finely divided

zinc oxide as a sensitiser. We have observed that zinc oxide behaves as a very powerful sensitiser for several photochemical reactions.

In previous papers (*Zeit. anorg. Chem.*, 1924, **134**, 172 ; *Jour. Phys. Chem.*, 1925, **29**, 926), we have shown that the velocity of sugar inversion in presence of acids is markedly accelerated by light and that inversion of cane-sugar takes place in sunlight even in the absence of acids. We have now observed that sugar inversion and hydrolysis of maltose can be markedly accelerated by sunlight in presence of zinc oxide as a sensitiser.

The following reactions have been found to be sensitised by zinc oxide in presence of sun light :—(1) Decomposition of Fehlings' solution ; (2) decomposition of cupri-ammonium oxalate ; (3) formation of reducing sugars from formaldehyde ; (4) formation of reducing sugars from glycerol; (5) oxidation of methyl or ethyl or propyl alcohol to the respective aldehyde by air; (6) formation of metallic gold from gold chloride; (7) formation of metallic platinum from platinic chloride ; (8) oxidation of quinine sulphate by chromic acid ; (9) oxidation of potassium iodide by potassium persulphate; (10) oxidation of sodium citrate by iodine ; (11) oxidation of oxalic acid by iodine; (12) oxidation of potassium tartrate by iodine; (13) hydrolysis of maltose; (14) oxidation of sodium formate by iodine ; (15) oxidation of iodoform ; (16) oxidation of potassium tartrate by bromine ; (17) oxidation of sodium nitrite by iodine ; (18) oxidation of hydroxylamine hydrochloride by iodine ; (19) oxidation of hydrazine hydrochloride by iodine ; (20) oxidation of sodium formate by mercuric chloride ; (21) oxidation of sodium sulphite by mercuric chloride ; (22) oxidation of hydrazine hydrochloride by mercuric chloride ; (23) oxidation of $(NH_4)_2C_2O_4$ by mercuric chloride ; (24) oxidation of potassium tartrate and mercuric chloride ; (25) oxidation of sodium malate and mercuric chloride ; (26) oxidation of potassium citrate and mercuric chloride; (27) oxidation of sodium lactate and mercuric chloride ; (28) oxidation of sodium dichlor-acetate and mercuric chloride ; (29) decomposition of mercuric oxide ; (30) decomposition of aqueous solutions of $KMnO_4$; (31) decomposition of potassium oxalate ; (32) decomposition of aqueous solution of potassium persulphate.

The following reactions are also sensitized by substances other than ZnO but in all the reactions ZnO is the best sensitiser.

(1) Potassium tartrate and $HgCl_2$—acceleration by ferric and ferrous chloride, $KMnO_4$, uranium nitrate and Al_2O_3.

(2) Sodium formate and HgCl₂.—in presence of Al₂O₃ and MnO₂. .

(8) Ammonium malonate+HgCl₂.—in presence of Al₂O₃.

(4) Sodium malate+HgCl₂.—in presence of Al₂O₃.

(5) Hydrazine hydrochloride+HgCl₂.—in presence of Al₂O₃ and erythrosin.

We have also investigated the effect of zinc oxide on the decolourisation of solutions of dyes when exposed to sunlight. The solutions of the dyes were exposed to sunlight in dishes in presence of air. The concentrations of the dye solutions were obtained from the measurements of the extinction coefficients.

To determine the extinction coefficient the dye was kept in a glass cell and placed before a Nuttings spectro-photometer and the absorption was read on the density scale of the instrument. Knowing the thickness of the cell, the extinction coefficient was calculated by the formula, $\text{Extinction coeff.} = \dfrac{\text{Density Reading}}{\text{Thickness}}$

10 c.c. taken in a glass dish: 0·1 gm. of ZnO was added.

No.	Dyes	Region in Å Units.	Time. H. M.	Extinction coeff. unexposed (dark).	Extinction coeff. exposed (sunlight).	Extinction coeff. exposed with ZnO (sunlight).
A.	BLUE, VIOLET AND GREEN.					
1	Crystal Violet Do. +ZnO	5560	1—30	2·753	2·624	0·130
2	Methylene Blue Do. +ZnO	5560	1—0	1·065	0·805	Bleached.
8	Ethyl Green Do. +ZnO	5560	1—30	2·233	2·104	0·130
4	Nile Blue Do. +ZnO	5560	1—0	1·065	1·064	Bleached.
5	Azolitmin Do. +ZnO	5840	1—0	1·351	1·299	0·005.

No.	Dyes.	Region in Å units.	Time H. M.	Extinction coeff. unexposed (dark).	Extinction coeff. exposed (sunlight).	Extinction coeff. exposed with ZnO (sunlight).
6	Aniline Blue Do. + ZnO	5880	1—0	5·558	2·442	0·397
7	Nigrosin Do. + ZnO	5840	1—0	1·299	1·299	0·130
8	Genatian Violet Do. + ZnO	5700	1—0	1·584	1·065	0·005
9	Malachite Green Do. + ZnO	5840	1—0	2·078	2·078	0·312
10	Methyl Violet Do. + ZnO	5040	1—0	0·805	0·727	0·104
11	Indigo Carmine Do. + ZnO	5040	1—0	0·779	0·779	0·156
12	Water Blue Do. + ZnO	5589	1—0	1·091	1·040	0·935
13	Allizarin Blue Do. + ZnO	5240	1—0	4·571	4·831	4·468
14	Cupric Blue Do. + ZnO	5360	1—0	1·351	1·247	0·935
15	Aniline Victorian Blue Do. + ZnO	5240	1—0	2·857	2·837	1·091
B.	FLOURESCENT DYES.					
16	Eosin Do. + ZnO	5520	1—45	1·506	0·571	0·026
17	Flourescein Do + ZnO	5200	1—45	1·114	0·649	0·104
18	Rhodamine Do + ZnO	5640	1—45	1·974	1·948	0·519
19	Erythrosine Do + ZnO	5480	1—45	3·636	2·206	0·727

No.	Dyes.	Region in Å units.	Time H. M.	Extinction coeff. unexposed (dark).	Extinction coeff. exposed (sunlight).	Extinction coeff. exposed with ZnO (sunlight).
20	Uranine } Do. + ZnO	5360	1—45	1·117	1·065	0·779
21	Pyronine G. } Do. + ZnO	5360	1—45	2·441	2·208	2·078
22	Acridine Red } Do. + ZnO	5360	1—0	1·714	1·688	0·883
C.	RED YELLOW AND ORANGE.					
23	Rose Bengale } Do. + ZnO	5920	2—30	1·506	1·351	1·273
24	Congo-Red } Do. + ZnO	5840	2—30	1·558	1·558	0·967
25	Aurine } Do. + ZnO	5680	1—0	1·247	0·935	0·519
26	Magenta } Do. + ZnO	5840	1—0	1·818	1·091	0·753
27	Aniline Red } Do. + ZnO	6160	1—0	2·203	1·091	1·040
28	Aniline yellow } Do. + ZnO	5120	1—0	2·078	1·974	0·312
29	Auramine } Do. + ZnO	4480	1—0	1·040	0·984	0·984
30	Methyl Orange } Do. + ZnO	5040	1—0	2·727	2·857	1·948
31	Purpurin } Do. + ZnO	5589	1—0	1·402	0·883	0·364
32	Tropaeolin } Do. + ZnO	5560	1—0	0·779	0·727	0·519

No.	Dyes.	Region in A units.	Time H. M.	Extinction coeff. unexposed (dark).	Extinction coeff. exposed (sunlight).	Extinction coeff. exposed with ZnO (sunlight).
33	Aniline Scarlet Do. + ZnO	5720	1—0	1·298	1·194	1·091
34	Theonine Grubber Do. + ZnO	5360	1—0	1·039	·984	·883
35	Thioflavine Do. + ZnO	5360	1—0	4·675	1·558	1·039
36	Corcus Red Do. + ZnO	5240	1—0	1·091	·678	·623
37	Rosaniline Do. + ZnO	5240	1—0	1·195	1·039	2·337*
38	Acridine Orange Do. + ZnO	5360	1—0	2·340	2·078	1·948
39	Acridine Yellow Do. + ZnO	5360	1—0	1·299	1·195	·987
40	Aesculin Do. ZnO	5360	1—0	1·649	·597	·416

With alizarin blue and methyl orange, there is a slight increase in the concentration of the solutions after exposure to sunlight. This is due to the fact that these dyes are not oxidized at all by air in presence of sunlight and a little water is lost by evaporation from the solutions after exposure to air for an hour.

In diffused light there was no change in the colour of the dyes with zinc oxide. The bleaching of the dyes was noticeable in a short time when the solutions were exposed to sunlight with zinc oxide.

As a general behaviour it was found that the dyes which absorb light of longer wave-lengths and are of the type blue, green, violet, etc., are much accelerated in their bleaching in sunlight by zinc oxide. The next in order comes the fluorescent dyes which also absorb light of longer wave-lengths, and lastly are the dyes of red,

orange and yellow type which absorb light of shorter wave-lengths. There are only very few exceptions to the above generalisation which might be due to impurities.

In recent papers Baur and co-workers (*Helv. Chim. Acta.*, 1924, **7**, 910 ; *Trans. Faraday. Soc.*, Oct. 1925, p. 629) have investigated the sensitising influence of zinc oxide on the photochemical decomposition of an aqueous solution of silver nitrate and methylene blue in absence of air.

In the case of the decomposition of silver nitrate, Baur and Perret (*loc. cit.*) represented the process schematically as follows :—

$$ZnO \begin{cases} \oplus + AgNO_3 + OH' \longrightarrow \text{Peroxide} \longrightarrow \text{Oxygen.} \\ \ominus + Ag^{\cdot} \longrightarrow Ag. \end{cases}$$
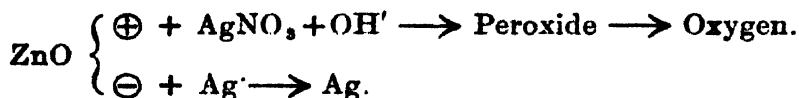
We are of the opinion that this scheme of Baur is unsatisfactory, because there is no experimental evidence in support of the above views, and the decomposition of silver nitrate can be easily understood from the following considerations :—It is well known that salts of heavy metals like silver, gold, platinum etc., have a tendency to decompose and in presence of light, solutions of these salts decompose readily. In presence of zinc oxide this decomposition tendency of silver nitrate is increased.

We are of opinion that in presence of light the molecules of zinc oxide absorb the incident radiation and become activated. The activated molecules of zinc oxide come in contact with the molecules of silver nitrate and activate them by the transference of energy from the molecules of zinc oxide to those of silver nitrate. The decomposition of silver nitrate takes place according to the following equation :—

$$2\,AgNO_3 + H_2O \rightleftharpoons 2\,Ag + 2\,HNO_3$$
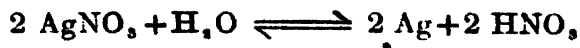
In addition to the sensitising effect, zinc oxide has also the function of neutralising the nitric acid which is set free and thus helps the decomposition of silver nitrate. We have observed that in presence of calcium carbonate, strontium carbonate etc., which also neutralise the free nitric acid, solutions of silver nitrate appreciably decompose in sunlight, but the effect of calcium carbonate, or strontium carbonate is not as great as that of zinc oxide which also acts as a marked photochemical sensitiser.

In a recent paper Chakravarti and Dhar (*Zeit. anorg. Chem.*, 1925, 142, 299) have shown that solutions of dyes are unstable in presence of light and they can be readily oxidised or reduced under suitable conditions. We have shown that in presence of air several dye solutions are readily oxidised in presence, of light, and in this paper we have shown that this oxidation of dyes is markedly accelerated by zinc oxide. Moreover in the same paper Chakravarti and Dhar proved that the solutions of dyes can also decompose in presence of strong ultra-violet or sunlight just as solutions of potassium permanganate, potassium persulphate or ammonium nitrite decompose in presence of strong light. In this paper we have proved that the decomposition of potassium permanganate, potassium persulphate etc., in sunlight is accelerated by zinc oxide.

Baur has represented the photolysis of methylene blue in presence of zinc oxide when air is not present in the following way :—

$$ZnO \begin{cases} \oplus + \text{methylene blue} \longrightarrow \text{products of oxidation.} \\ \ominus + \text{methylene blue} \longrightarrow \text{leuco compounds.} \end{cases}$$
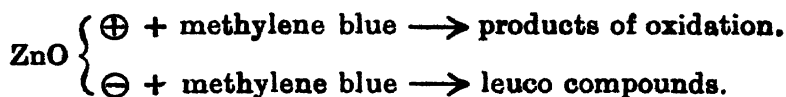
We are however of the opinion that these dyes which are unstable substances decompose in sunlight in the same way as the solution of potassium permanganate does in sunlight. It is likely that the decomposition of dyes can in some cases be compared to the decomposition of nitrous acid, hypophosphorous· acid, phosphorous acid etc., according to the following equations :—

$$3\ HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$$

$$4\ H_3PO_3 \rightleftharpoons 3H_3PO_4 + PH_3$$

$$2\ H_3PO_2 \rightleftharpoons H_3PO_4 + PH_3$$

The photochemical decomposition of nitrogen pentoxide has been found by Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, 43, 53, 72) to be accelerated in visible light in presence of nitrogen dioxide. We are of opinion that nitrogen dioxide acts as a sensitiser in the photochemical decomposition of nitrogen pentoxide, just as chlorine sensitises the photochemical decomposition of ozone.

Further work on photo-sensitisation and photo-inhibition is in progress in these laboratories.

An Experimental Contribution to the Theory of Equation of State for Adsorbed Substances.

By Hira Lal Roy.

If one considers with Langmuir $(\sigma_0 - \sigma) = \pi$ as the two dimensional osmotic pressure of the dissolved substance on the surface, then according to Volmer (*Zeit. physikal. Chem.*, 1925, 250, *cf.* also Adams, *Proc. Roy. Soc.*, 1922, A 101, 526), one can deduce a characteristic equation for adsorbed substances which from the measurements of adsorption of benzophenone on mercury has been found to take the following form :

$$\pi\,(\Omega - \beta) = RT \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1)$$

where $\Omega =$ the surface which contains a gram molecule of the dissolved capillar-active substance.

$\beta =$ a correction-factor, *i.e.*, twice the surface actually occupied by a gram-molecule of the dissolved substance.

Assuming $\dfrac{\beta}{\Omega}$ to be very small compared to 2, Volmer (*loc. cit.*) also obtained the following relation between π and c :—

$$\pi = \frac{RTc}{k + \beta c} \qquad \ldots \qquad \ldots \qquad \blacksquare \qquad (2)$$

$$\epsilon = \frac{1}{\Omega} = \frac{c}{k + 2\beta c} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (3)$$

Integrating the well known Gibb's equation (Milner, *Phil. Mag.*, 1907, **23**, 96) one obtains the following equation which has already been found empirically by Szyzkowski (*Zeit. physikal. Chem.*, 1908, **64**, 392) :—

$$\pi = \frac{RT}{2\beta}\, ln\left(\frac{2\beta c}{k} + 1 \right) \qquad \ldots \qquad \ldots \qquad (4)$$

4

If one accepts equation (1) to be sufficiently correct, then equations (3) and (4) assume the character of approximations. If equation is

used without neglecting the higher powers of $\left(\dfrac{\beta}{\Omega} \right)$, then we have, from (1) and the Gibb's equation,

$$\mathrm{RT}\frac{dc}{c} = \mathrm{RT}\frac{d\pi}{\pi} + \beta d\pi,$$

which on integration gives

$$\mathrm{RT}\, lnc + \beta = \mathrm{RT}\, ln\, \pi + \beta\pi \qquad \ldots \qquad \ldots \qquad (5)$$

The present work deals with general validity of equation (2) which has been found to hold good in the case of saturation of mercury with benzophenone.

<div align="center">EXPERIMENTAL.</div>

The surface tensions were measured by a modified form of the method used by Sugden (*J. Chem. Soc.*, 1921, **121**, 1). [Schroedinger equation (*Ann. Phys.*, 1915, [IV], **45**, 413)].

A capillary tube (K) with the end cut as sharply as possible is dipped in the liquid, and the maximum pressure of the gas (air or a suitable indifferent gas) at the exit of the bubble is measured. A sketch of the arrangement used is given in Fig. I.

P and G contain the solution and W contains water. Behind the vertical U-tube M, containing a dilute coloured solution is attached a millimeter scale to read the difference in level between the two arms of the tube. The height of the solution above the capillary end K is read with a cathetometer. G is detachable at S and R being provided with ground in glass joints. The capillary tube is fused into a wider tube which fits exactly into the ground in joint at R. When cock L is closed and H opened, water flows out of W, a partial vacuum is created and air enters into P gets saturated with the vapour of the solution, and bubbles through the capillary tube. The maximum pressure difference is proportional to $h = h_m - h_s$ where $h_m =$ the reading of water manometer and $h_s =$ height of the solution as measured by the cathetometer. The capillary-end must be made as far as possible circular in shape and very sharply cut. The diameter as measured by micrometer was found to be about 0·0048. cm.

FIG.

Scale.

Cathetometer.

Thermometer.

air
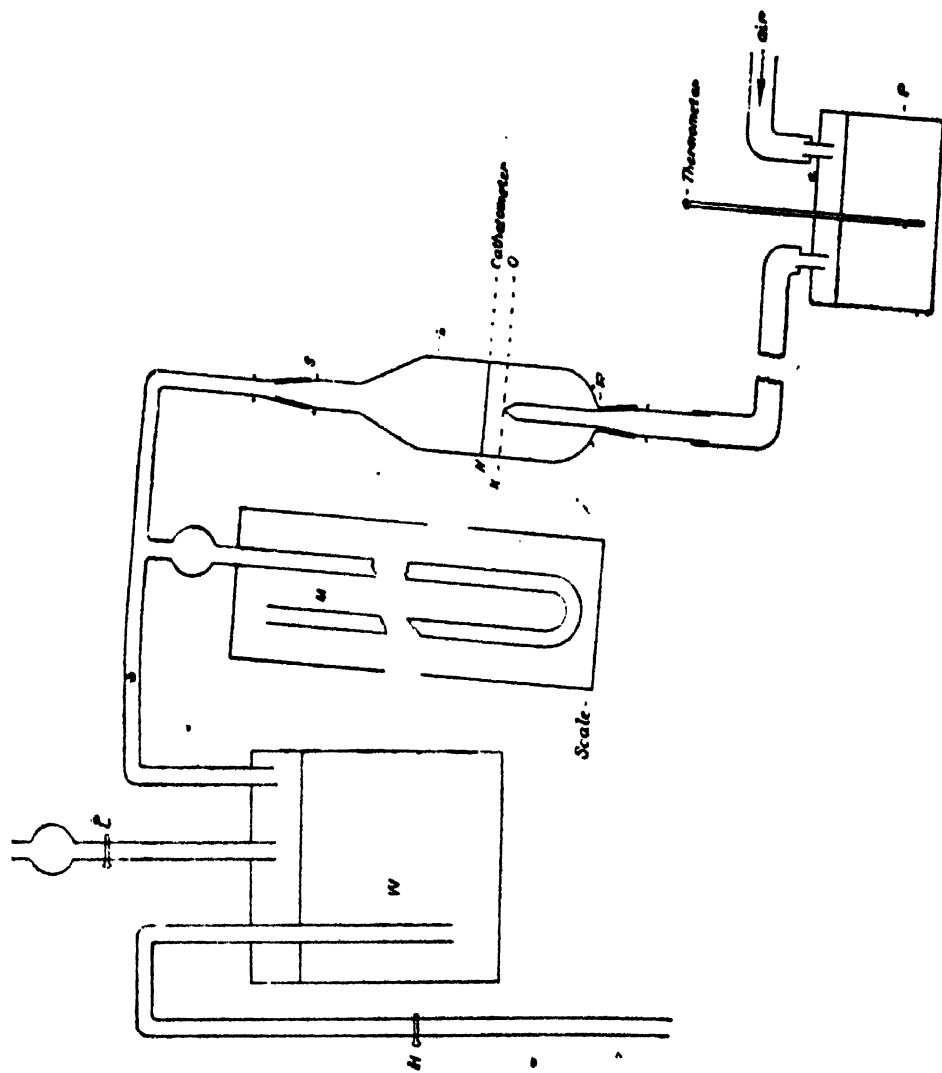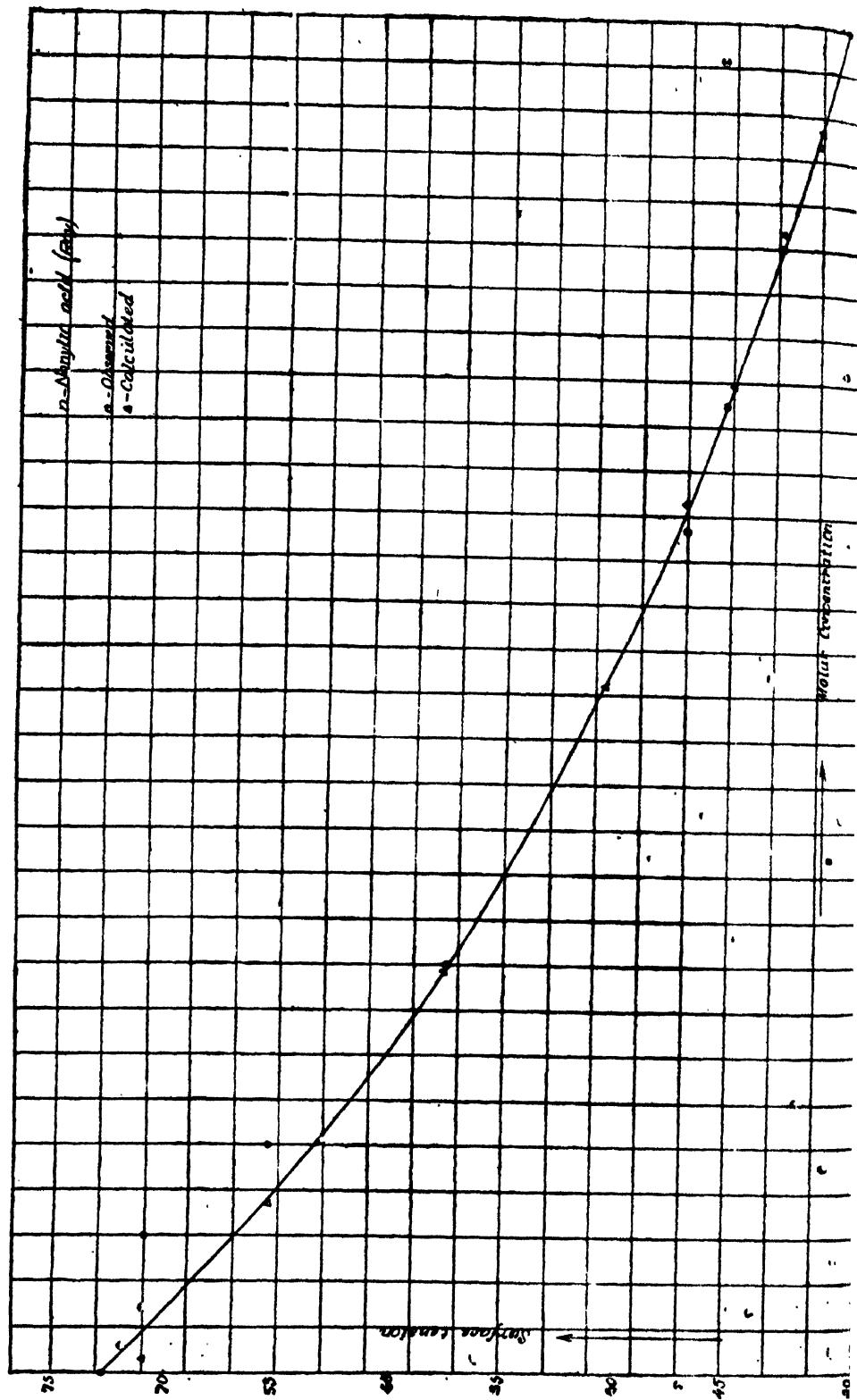
To ascertain that the capillary opening has not been enlarged by gradual solution of the glass or narrowed down by any impurity, measurements of the surface tension of pure water and benzene are carried out before every series of experiments. A new capillary made and its shape and diameter measured where necessary. The smallness of the capillary allowed a level-difference, h_m of 480 to 630·5 mm. and under these circumstances, the terms containing the factor (r/h) in Schroedinger's equation may be neglected.

But in the case of solutions of capillar-active substances the maximum pressure sinks slowly down, while the number of bubbles coming out per unit time decreases. If the air within the bubble is assumed to be saturated with the vapour of the solution, the cause for this slow establishment of equilibrium must be attributed to the fact that the formation of the bubble dilutes the surrounding solution through adsorption of the solute and the next bubble has a poorer solution around it. The original concentration is reached slowly as is well known. Similar relations have been observed in the case of drop-electrodes. In every case readings were taken with decreasing number of bubbles in a given interval and the limiting value for infinitely slow formation of bubbles was obtained by extrapolation.

In this work ordinary distilled water has been used throughout. The chemicals used in this investigation were obtained from Kahlbaum. The fatty acids were subjected to fractional distillation and their purity tested.

Results and Discussions.

Volmer (*loc. cit.*) states that at small concentrations equations (2) and (4) are identical. Equation (4) may be written as :—

$$\pi = \frac{RT}{2\beta} \, ln \left(\frac{2\beta c}{k} + 1 \right)$$

$$= \frac{RT}{2\beta} \left[\frac{2\beta c}{k} - \tfrac{1}{2}\left(\frac{2\beta c}{k} \right)^{2} + \tfrac{1}{3}\left(\frac{2\beta c}{k} \right)^{3} \cdots\cdots\cdots \right]$$

$$= \frac{RTc}{k\left(1+ \frac{\beta c}{k}\right)} + \frac{RTc}{k} \left[\tfrac{1}{3}\left(\frac{\beta c}{k} \right)^{2} \cdots\cdots\cdots\cdots\cdots\cdots \right]$$

$$= \frac{RTc}{k+\beta c} + \frac{RTc}{k} \left[\tfrac{1}{3}\left(\frac{\beta c}{k} \right)^{2} \cdots\cdots\cdots\cdots\cdots \right].$$

If $\dfrac{\beta c}{k}$ be not very small, then the values of π according to (4) are greater than those derived from (2). In the following Tables (I-VI), π is calculated by a method of approximation (to be discussed later) according to both these equations. The surface tensions are expressed in dynes cm. and concentration in gram-mol litre.

TABLE I.

n-*Butyric Acid.*

(Szyzkowski—20°)

$$\beta = 5\cdot82 \times 10^6 \; ; \; k = 1\cdot5 \times 10^8 \; ; \; T = 72\cdot66.$$

Concentration.	π observed.	π calc. (Eq. 2).	π calc. (Eq. 4).
0·0242	4·36	4·55	4·56
0·0363	6·50	6·47	6·54
0·0545	9·01	9·03	9·15
0·0917	12·21	12·28	12·56
0·122	15·81	15·92	16·77
0·184	19·95	20·17	21·95
0·276	24·27	24·3	27·8
0·414	28·92	28·3	34·4
0·6205	33·75	31·7	41·4

TABLE II.

n-*Valeric Acid* (17·5°).

$$\beta = 4\cdot65 \times 10^6 ; \; k = 0\cdot394 \times 10^8 ; \quad T = 72\cdot9.$$

Concentration.	π observed.	π calc. (Eq. 2).	π calc. (Eq. 4).
0·0093	5·1	5·14	5·18
0·014	7·4	7·36	7·46
0·021	10·8	10·6	10·74
0·0315	14·5	14·05	14·57
0·0475	18·95	18·7	19·72
0·071	23·8	23·7	25·76
0·107	28·2	29·0	33·2
0·160	33·2	33·9	41·0
0·240	38·3	38·5	49·6

TABLE III.

n-*Hexylic Acid.*

$t = 18° - 19°$; $\delta_0 = 72 \cdot 66$; $\beta = 4 \cdot 3 \times 10^5$; $k = 0 \cdot 129 \times 10^5$.

Concentration.	π observed.	π calc. (Eq. 2).	π calc. (Eq. 4).
0·00425	9·16	6·98	6·95
0·0064	9·66	9·9	9·97
0·0085	12·56	12·45	12·55
0·0128	17·26	16·85	17·24
0·0170	21·01	20·4	21·22
0·0212	23·66	23·32	24·63
0·0256	25·84	25·96	27·83
0·0340	29·91	29·99	33·1
0·0425	32·86	33·0	37·58
0·051	35·41	35·5	41·45
0·068	38·46	39·2	47·83
0·085	41·86	41·7	53·04

TABLE IV.

n-*Heptylic Acid.*

$t = 19° \cdot C$, therefore $\delta_0 = 72 \cdot 66$; $\beta = 4 \cdot 74 \times 10^5$; $k = 0 \cdot 0291 \times 10^5$.

Concentration.	π observed.	π calc. (Eq. 2).	π calc. (Eq. 4).
0·001059	5·96	7·52	7·92
0·00254	14·91	14·98	15·85
0·00381	19·76	19·6	20·65
0·004887	22·79	22·7	24·34
0·00588	24·96	25·03	27·3
0·00678	26·76	26·82	29·5
0·007775	28·46	28·6	32·3
0·008825	30·06	30·12	34·6
0·01089	32·56	32·4	38·2

TABLE V.

n-*Octylic Acid.*

t=24°C, therefore δ_0=71·93; $\beta=4\cdot105\times10^8$; $k=0\cdot01016\times10^8$

Concentration.	π observed.	π calc. (Eq. 2).	π calc. (Eq. 4).
0·0003361	6·43	7·18	7·3
0·0006722	13·43	13·03	13·13
0·0010083	17·58	17·4	18·12
0·001344	21·03	21·18	22·24
0·001680	23·93	24·3	26·0
0·0020166	26·48	27·0	29·3
0·002352	28·9	29·33	32·25
0·002688	31·18	31·3	35·0
0·003025	33·23	33·1	37·5
0·003361	34·83	34·64	39·8

TABLE VI.

n-*Nonylic Acid.*

t=19°C, therefore $\delta_0=72\cdot66$; $\beta=3\cdot61\times10^8$; $k=0\cdot00286\times10^8$.

Concentration.	π observed.	π calc. (Eq. 2).	π calc. (Eq. 4).
0·0001520	9·16	10·88	10·96
0·0002298	15·03	15·2	15·4
0·0003882	22·04	22·02	22·95
0·0004778	25·58	25·8	26·6
0·000546	27·39	27·4	29·3
0·000637	29·94	29·93	32·3
0·0007645	33·03	33·0	36·2
0·000695	31·48	31·4	34·0

From these tables we see that (2) and (4) are practically identical at small concentrations, but at higher concentrations they differ from one another.

In fact $\left(\dfrac{\beta c}{k}\right)$ reaches values greater than 1 at higher concentrations, and therefore in those cases the equations are not applicable. Table VII in which values of $\left(\dfrac{\beta c}{k}\right)$ for two approximately equal values of π are given, will make it clearer.

TABLE VII.

Substance.	$\beta \times 10^{-3}$	$k \times 10^{-3}$	$\frac{\beta c}{k}$					
			(Conc.)$_1$	π_1	$\left(\frac{\beta c}{k}\right)_1$	Conc. $_2$	π_2	$\left(\frac{\beta c}{k}\right)_2$
n.Butyric acid	5·82	1·15	0·0363	6·5	0·184	0·6205	33·75	3·14
n-Valeric acid	4·65	0·394	0·0093	5·1	0·1099	0·160	33·2	1·86
n-Hexylic acid	4·3	0·129	0·00425	6·16	0·1415	0·0425	32·86	1·415
n-Heptylic acid	4·74	0·0291	0·001059	5·96	0·1448	0·01089	32·56	1·53
n-Octylic acid	4·105	0·01016	0·0003361	6·43	0·1357	0·003025	33·23	1·223
n-Nonylic acid	3·61	0·00286	0·000152	9·16	0·193	0·0007645	33·03	0·965

In the case of higher fatty acids with little solubility the agreement between these two equations for all concentrations is certainly better but still not satisfactory.

The area occupied by the molecules adsorbed on the surface can be calculated from the above only from the observations at low concentrations. Such observations are not however as accurate as those at higher concentrations. Moreover, at very low concentrations, where in the adsorption layer the ideal gas laws almost hold good, the influence of β is negligible and consequently it cannot be measured accurately. The actual area occupied by the molecule was for these reasons calculated according to the more rigorous equation. For the calculation of a and β, the following method of approximation was used:

First of all, from the measurements at two successive concentrations β was calculated according to the equation,

$$\beta_1 = \frac{RT}{\pi_2 - \pi_1} \; ln\left(\frac{c_2\,\pi_1}{c_1\,\pi_2}\right).$$

then from all these values of β_1, the mean value β_2 was taken. With this β_2, from the following equation, the values of a was calculated.

$$a = RT \; ln \frac{\pi}{c} + \beta_2 \pi$$

From these values of a, the mean value a_s was taken and then the mean value of β (β_s) was once more calculated.

From these values of a and β the corresponding concentrations were calculated from the observed values of π according to equation

$$ln c = \frac{RT \ln \pi + \beta_s \pi - a_s}{RT}$$

and the differences were graphically determined.

It is found that the values of π thus calculated show good agreement with those obtained for the following solutions : (1) acetic acid, propionic acid (Drucker, *Zeit. physikal. Chem.*, 1905, **52**, 648) ; (2) propionic acid (Rehbinder, *ibid*, 1924, **111**, 447) ; (3) *n*-butyric acid, *n*-valeric acid, *n*-hexylic acid (Szyzkowski, *loc. cit.*); (4) *n*-heptylic acid, *n*-octylic acid, *n*-nonylic acid (Roy, *vide supra*).

We have also determined the surface tension of solutions of the substances mentioned in the following tables where the values of π observed with those calculated from equation (5) are also given :

TABLE VIII.

Monomethylurea.

$$t = 21°C; \; a = 2.2445 \times 10^{10}; \; \beta = 12.24 \times 10^{4}.$$

Conc.	σ obs.	π obs.	π calc.	Conc. calc.
0.00	72.37	0.00	...	...
1.238	69.6	2.77	2.77	1.267
1.63	68.93	3.44	3.54	1.628
2.09	68.12	4.25	4.25	2.088
2.61	67.3	5.07	5.07	2.608

TABLE IX.

Symmetrical Dimethylurea.

$t = 20°C$; $\alpha = 5·06 \times 10^{10}$; $\beta = 18·5 \times 10^{5}$.

Conc.	σ obs.	π obs.	π calc.	Conc. calc.
0·00	72·53	0·00	...	...
0·2675	70·3	2·23	2·03	0·2953
0·535	69·2	3·33	3·38	0·5354
0·767	68·2	4·38	4·38	0·753
1·0704	67·0	5·53	5·63	1·049
1·504	65·5	7·03	7·03	1·503
1·935	63·6	8·93	9·06	2·096

TABLE X.

Ethylurea.

$t = 19·5°C$; $\alpha = 6·29 \times 10^{10}$; $\beta = 9·04 \times 10^{5}$.

Conc.	σ obs.	π obs.	π calc.	Conc. calc.
0·00	72·66	0·00	...	...
0·2735	69·6	3·06	3·2	0·2524
0·547	66·85	5·75	5·85	0·4947
0·82	64·5	8·1	8·1	0·825
1·23	61·4	11·2	10·9	1·276
1·846	58·0	14·6	14·3	1·895
2·585	55·1	17·5	17·6	2·52

TABLE XI.

Symmetrical Diethylurea.

t = 19·5°C; a= 10·14 × 10¹°; β= 14·7 × 10ˢ.

Conc.	σ obs.	π obs.	π calc.	Conc. calc.
0·00	72·6	0·00	...	...
0·0451	70·0	2·6		0·0468
0·09025	67·9	4·7		0·096
0·1805	65·4	7·2		0·1706
0·2344	63·7	8·9	Almost the	0·235
0·305	62·15	10·45	same values as those	0·3023
0·4032	60·32	12·28	observed.	0·3966
0·524	58·4	14·2		6·516
0·681	56·15	16·45		0·683
0·8173	55·2	18·4	18·0	0·861

TABLE XII.

Phenol.

t = 19°C; a = 12·8 × 10¹°; β = 10·24 × 10ˣ.

Conc.	σ obs.	π obs.	π calc.	Conc. calc.
0·00	72·66	0·00	...	...
0·02505	69·75	2·91	4·26	0·0166
0·0501	66·4	6·26	7·26	0·0413
0·084	62·1	10·56	10·56	0·0834
0·1002	60·7	11·76	11·96	0·1000
0·1252	58·9	13·96	13·76	0·1247
0·1606	56·6	16·06	16·06	0·1509
0·1841	65·2	17·46	17·46	0·1802
0·2087	63·6	19·06	18·76	0·2155
0·2504	51·2	21·46	20·66	0·2706
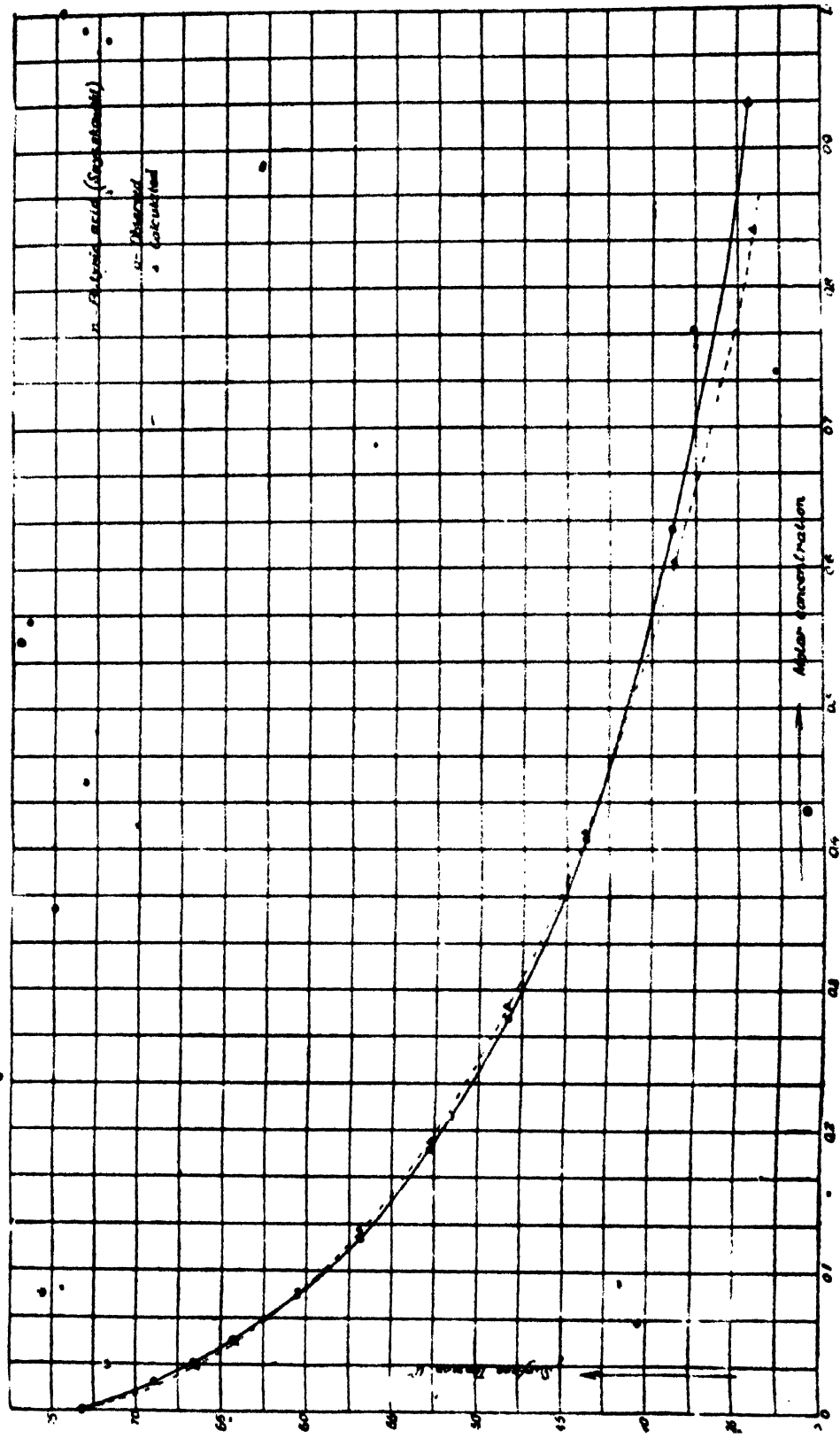
Fig. 3.

From the above we see that in the case of lower fatty acids, the agreement between the values calculated according to the equation (5) and those observed are satisfactory up to middle concentrations. For the higher homologues with decreasing solubility the agreement between these values are satisfactory up to the highest concentrations studied. Also we find that in the case of the higher fatty acids, no matter according to which equation the values of π are calculated, the tension at lower concentrations are always greater than those calculated (*vide* Fig. 2, for *n*-butyric and *n*-nonylic acid). The (σ, conc.) curve has bend in that region. This anomaly which has also been noticed by Lord Raleigh (*Phil. Mag.*, 1889, **48**, 381) and Langmuir cannot possibly be due simply to errors in experiments. That this effect depends only on the electrolytic dissociation, which at smaller concentrations must reach its maximum, appears also doubtful.

The equations derived in the introduction contain definite physical significance through the experimentally settled fact that the adsorption-layer is only one molecule thick. On this assumption β of Van der Waal's equation is to be considered in this case as double the cross-section of the adsorbed molecule. The molecular cross sections (f) as calculated from the experimental results are put together in the following table :—

$$f = \frac{\beta}{2N}, \text{ where } N = 6 \cdot 06 \times 10^{33}$$

TABLE XIII.

			$\beta \times 10^{-8}$ (Eq. 5)	$f \times 10^{16}$
Acetic acid	...	...	16·4	13·52
Propionic acid	...	...	13·9.;	11·51
n-Butyric acid	...	...;	10·7	8·83
n-Valeric acid	...	...	10·01	8·26
n-Hexylic acid	...	...	10·4	8·58
n-Heptylic acid	...	...	10·04	8·3
n-Octylic acid	...	...,	7.54	6·26
n-Nonylic acid	...	...	6·00	4·95
Monomethyl urea	...	...	12·24	10·1
Symmetrical dimethyl urea	...	...	18·5	15·25
Ethyl urea	...	...	11·25	9·28
Symmetrical diethyl urea	...	...	14·7	12·12
Phenol	...	...	10·24	8·45

From Table XIII we observe that the effective molecular cross section of the normal fatty acids in the adsorption layer does not increase with increasing molecular weights. Langmuir thinks that this constant magnitude of the area occupied by the fatty acids is to be explained by the vertical position of the carbon chain in the

surface. This supposition is more strikingly confirmed by our results with urea derivatives. If one agrees with Langmuir and Harkins that the group containing oxygen is directed downwards in the water while the hydrocarbon groups are pointed towards surface, one can easily explain the increase of the value of f when one passes from monomethylurea to s-dimethylurea. Then the values of (f) in the case of methylurea and ethylurea must also be the same, which agrees with our experimental results.

The term a has the same significance as an integration constant as the term k in the equation (2) *i.e.*, it controls the distribution relation between the number of molecules in the solution and in the surface. One can certainly according to the method of Langmuir convince oneself of this that a differs from the adsorption potential A by the same additive constant for all substances dissolved in the same solvent, the magnitude of which depends on the thickness of the adsorption layer.

Langmuir has drawn our attention to the fact that Traube's Law is equivalent to the increase of the adsorption potential in the arithmetic progression, if the area occupied by the molecule in the homologous series is constant. We find in our experimental results a further confirmation of Traube's Law. But it remains as yet unexplained, why A increases by the same amount as we go up in the homologous series (*vide* Table XIII.) We would venture a suggestion that because of the polar character of the fatty acids, the adsorption potential must be proportional to the dipol-moment of the molecule, and therefore increases by jumps with the length of the carbon chain as would appear from Table XIV.

TABLE XIV.

			$a \times 10^{-10}$ (Eq. 5)	$\Delta a \times 10^{-10}$
Acetic acid	...	...	8·75	
				2·15
Propionic acid	...	...	11·30	
				2·05
n-Butyric acid	...	...	13·35	
				2·88
n-Valeric acid	...	...	16·23	
				3·17
n-Hexylic acid	...	...	19·40	
				3·3
n-Heptylic acid	...	...	22·7	
				2·72
n-Octylic acid	...	...	25·42	
				2·36
n-Nonylic acid	...	...	27·78	

From these investigations we can conclude that the equation for adsorbed substances proposed by Volmer is applicable to solutions up to moderate concentrations within the range of experimental error and that this equation allows us with fair approximation to consider the area occupied by the molecules of the solute on the surface of the solution and also the adsorption potential as independent of concentration.

I take great pleasure in expressing my gratitude to Professor M. Volmer for his kind advice and encouragement in the carrying out of this work and also my thanks to my friends Dr. H. Cassel and Dr. G. Adhikari for their help.

Replacement of Sulphonic Groups by Nitro Groups in Aromatic Amino-compounds.

BY RASIK LAL DATTA AND PHULDEO SAHAY VARMA.

In a previous communication (Datta and Varma, *J. Amer. Chem. Soc.*, 1919, **41**, 2039) it has been shown that in a number of phenolic compounds, sulphonic groups could be easily replaced by nitro groups by means of nitrous gases and a number of nitro-phenolic compounds in a fair state of purity and in good yields were obtained by this method. It has been possible to extend this investigation further and we find that the replacement of sulphonic groups by nitro groups is a general reaction in the case of aromatic amino-compounds also. In this case not only the sulphonic groups are replaced by nitro groups but the amino group is at the same time diazotised and replaced by the hydroxyl group so that the final products of the reaction in this case also are nitro-phenolic compounds. The products are in this case also as in the previous one generally free from bye-products and as a rule more than one nitro-group enters into the benzene nucleus.

It is interesting to find that in the case of naphthylamine sulphonic acid, the replacement of the sulphonic group by the nitro group is not brought about, though the amino-group is diazotised and replaced by the hydroxyl-group and the compound is nitrated as well. Thus a nitro-naphthol sulphonic acid has been obtained from a solution in chloroform of naphthylamine sulphonic acid.

EXPERIMENTAL.

Sulphanilic Acid.—Sulphanilic acid (10 g.) was partly dissolved and partly suspended in water (100 c.c.) and nitrous gases (obtained from arsenous oxide and nitric acid) passed. The gases were completely absorbed at the outset. The sulphanilic acid in suspension gradually passed into solution and the colour of the solution changed to greenish. Minute bubbles of gases were observed to escape.

When no more of the gas was absorbed, the solution was evaporated on the water-bath to a viscous consistency. On allowing to cool the product solidified. It was separated from the mother-liquor and crystallised from alcohol. The crystals (90 g., m. p. 122°) were found to be 2 : 4 : 6-trinitro-phenol.

Aniline-disulphonic Acid.—Aniline-disulphonic acid (10 g.), partly dissolved and partly suspended in water, was subjected to the action of nitrous gases until no more gases were absorbed. The reacting mixture was concentrated on the water-bath and allowed to cool and stand overnight. No solid separated. It was diluted and neutralised with powdered barium carbonate. The solution was filtered, boiled with animal charcoal, again filtered and the filtrate heated with the requisite quantity of sulphuric acid. The barium sulphate was removed by filtration. The filtrate was now concentrated on water-bath to a small volume. On allowing to cool, crystals (4 g.) of 2 : 4 : 6-trinitro-phenol were obtained.

m-Aniline Sulphonic Acid.—This sulphonic acid was prepared by sulphonating nitrobenzene and reducing the resulting nitrobenzene sulphonic acid by means of iron-filings and sulphuric acid. *m*-Aniline sulphonic acid (5 g.) thus prepared was treated with nitrous gases for 30-40 minutes. The reacting solution was evaporated to about half the volume and allowed to cool and crystallise. Crystals (3 g., m. p. 150°) were obtained and found to be 2 : 5-dinitro-phenol.

p-Nitraniline Sulphonic Acid.—By sulphonatiug *p*-nitraniline, a sulphonic acid derivative was obtained. The solution of this product (5 g.) was subjected to the action of nitrous gases for about 20 minutes. Considerable frothing took place. The solution turned dark red. It was evaporated to half its volume, and the solid separated was crystallised from rectified spirit. Crystals of 2 : 4-dinitro-phenol, m. p. 112°, were obtained.

Dimethylaniline Sulphonic Acid.—By heating dimethylaniline (20 g.) with concentrated sulphuric acid at 180°-190° for three hours and a half, dimethylaniline sulphonic acid was obtained. The product so obtained was submitted to steam distillation to get rid of unchanged dimethylaniline. By concentrating the product a syrupy liquid was obtained. This was diluted with a small quantity of water and nitrous gases passed in a rapid stream for about 20 minutes. A copious yellow solid separated. It was removed, washed with water and crystallised from rectified spirit. Brownish

yellow shining crystals, m. p. 153° of 2:8:4-tri-nitrodimethyl amino-benzene were obtained. Yield 5·5 g.

o-*Toluidine-5-sulphonic Acid.*—This sulphonic acid was prepared and separated by the method of Gerver (*Annalen*, 1878, 169, 374). The solid product (10 g.) was dissolved in water and treated with nitrous gases until no more absorbed. The product obtained was separated and crystallised as usual. 3:5-Dinitro-o-cresol (5 g.) m. p. 86°, was obtained.

o-*Toluidine-3:5-disulphonic Acid.*—This was prepared by the method of Neville and Winther (*Ber.*, 1882, 15, 2992). The solid product was dissolved and treated in the same way as in the preceding case. 3:5-Dinitro-o-cresol (5 g.) from 8 g. of the disulphonic acid was obtained.

m-*Toluidine Sulphonic Acid.*—This was prepared by the method of Lorenz (*Annalen*, 1874, 172, 185) and treated with nitrous gases as before. On concentration and cooling a copious yellow precipitate was obtained. It was crystallised and found to be 2:4:6-trinitro-m-cresol (11·2 g.) from 10 g. of m-toluidine.

p-*Toluidine-3-sulphonic Acid.*—In this case if nitrous gases were passed for a long period, oxalic acid was the only product obtained. If however, care was taken in passing the gases for a few minutes only 3:5-dinitro-p-cresol was obtained. In 10 g. of the sulphonic acid, fifteen minutes of passing the gases are enough to produce 3:5-di-nitro-p-cresol (3 g.). The yield decreases as the nitrous gases are passed for a longer period. In about 45 minutes, there is no trace of the dinitro-cresol, but on concentrating the solution and allowing it to cool in a desiccator, crystals of oxalic acid only are obtained.

p-*Toluidine-3:5-disulphonic Acid.*—No nitro-derivative could be obtained from this substance. Crystals of oxalic acid only were obtained.

m-*Xylidine Sulphonic Acid.*—This solid compound was dissolved in water and nitrous gases passed until no more absorbed. Some yellow solid separated during the process. On concentration on water-bath and cooling more yellow solid producted separated. It was crystallised and found to 5-nitro-1:3:4-xylenol, m.p. 71-72°. (Found: N, 8·79. $C_8 H_9 O_3 N$ requires N, 8·39 per cent.).

6

A part of this work was done at the Chemical Laboratory of the Presidency College, Calcutta, and a part at the Chemical Laboratory of the Benares Hindu University.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

CHEMICAL LABORATORY,
HINDU UNIVERSITY, BENARES.

Thiosulphato-Cobalt Complexes. Part II.
Thiosulphato-pentacyano-potassium Cobaltiate.

By Priyada Ranjan Rây.

In a previous communication the preparations and properties of a number of thiosulphato-pentammine cobaltic salts have been described, in which the thiosulphate radicle is a member of the complex positive ion with cobalt as the central atom. Description of a compound in which the thiosulphate group is a constituent of a negative complex ion with cobalt as the central atom forms the subject-matter of the present paper. The action of potassium cyanide solution upon thiosulphato-pentammine cobaltic chloride (*loc. cit.*) has led to the formation of a new type of compound whose constitution can be represented as $K_4[S_2O_3 . Co (CN)_5]$.

This may be regarded as containing a substituted cobalticyanide ion and be termed thiosulphato-pentacyano-potassium cobaltiate. The complex ion thus derived has a negative valency of four and in fact is the first representative of the hitherto unknown type of the complex cobalt salts. Similar substituted ferro- and ferri-cyanides have, however, been described by Hoffmann. These are nitrito-, sulphito-, and arsenito-pentacyano ferroate (*Zeit. anorg. Chem.*, 1896, **12**, 167) ; nitroso-pentacyano-ferriate (*Annalen*, 1900, **312**, 1), and aquo-pentacyano-ferriate (*Zeit. anorg. Chem.*, 1896, **12**, 150).

The constitution of the above thiosulphato-pentacyano-cobaltiate has been definitely established by chemical and physical methods. The reaction leading to its formation may be expressed by the following equation :—

$$\left[S_2O_3.Co.(NH_3)_5\right]Cl + 5\,KCN = K_4\left[Co\,\begin{matrix}S_2O_3\\(CN)_5\end{matrix}\right] + KCl + 5\,NH_3$$
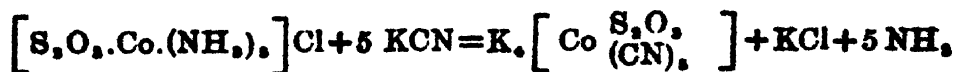
The action of sodium nitrite and sodium sulphite solutions upon the thiosulphato-pentammine cobaltic chloride has led to the formation of trinitrito-triammine cobalt and an impure mixture of sodium cobaltisulphite respectively as indicated below :—

$$\left[(NH_3)_5.Co.S_2O_3\right]Cl + 3\,NaNO_2 = \left[Co\,\begin{matrix}(ONO)_3\\(NH_3)_3\end{matrix}\right] + NaCl + Na_2S_2O_3 + 2\,NH_3$$

and

$$[(NH_3)_5\,Co\,S_2O_3]Cl + 3\,Na_2SO_3 = Na_3[Co\,(SO_3)_3] + NaCl + Na_2S_2O_3 + 5\,NH_3$$
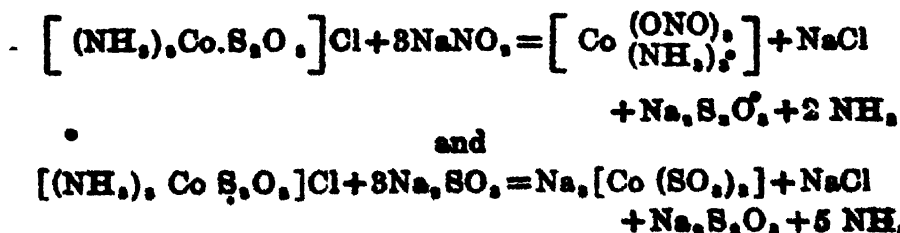
EXPERIMENTAL.

Preparation.—The thiosulphato-pentammine cobaltic chloride was finely powdered and treated with a strong solution of potassium cyanide ; there was a strong evolution of ammonia and a deep orange-coloured solution was obtained. The solution was filtered, cooled in ice water and then treated with alcohol drop by drop with constant stirring. A large crop of yellow crystals separated out in a short time. The crystals were filtered, washed with 30 per cent. alcohol and then redissolved in a small quantity of water. The solution was again cooled in ice water and the substance recrystallized by the addition of a few drops of alcohol. The crystals were first washed as before and then with absolute alcohol. They were finally dried in air.

The crystals thus obtained are bright yellow and highly soluble in water. The solution does not give any reaction for cobalt ions and is neutral to litmus. Neither sulphuretted hydrogen nor ammonium sulphide gives any precipitate of cobalt sulphide from its solution. Silver nitrate solution gives a yellow gelatinous precipitate in the cold, but on warming with dilute sulphuric acid it slowly changes into brown silver sulphide. A solution of the substance when boiled with dilute sulphuric acid or strong hydrochloric acid gives a precipitate of sulphur and liberates sulphur dioxide gas but no hydrocyanic acid. On oxidation with ammoniacal hydrogen peroxide the whole of the thiosulphate radicle is oxidized to sulphate without any change in the colour of the solution. A freshly prepared solution of the salt gives characteristic precipitates with solutions of salts of the heavy metals as described below—resembling potassium cobalticyanide very closely in this respect.

Silver nitrate solution gives a light yellow gelatinous precipitate in the cold, soluble in ammonia. Cobalt nitrate solution gives a rose-coloured gelatinous precipitate. Copper sulphate solution gives a light green gelatinous precipitate insoluble in dilute acids but soluble in ammonia to a blue solution. Lead nitrate solution gives a cream coloured heavy granular precipitate soluble in dilute acetic acid. With manganous chloride solution no precipitate is obtained—a distinction from potassium cobalticyanide. Mercuric chloride solution gives no precipitate whereas mercurous nitrate solution gives a pale yellow precipitate insoluble in dilute nitric

acid. With nickel sulphate solution a pale green gelatinous precipitate insoluble in dilute sulphuric acid is formed. Zinc sulphate solution gives a light yellow sparingly soluble precipitate which dissolves in hot water and forms a crystalline precipitate on cooling. Cadmium nitrate solution behaves like zinc giving a light yellow sparingly soluble precipitate. The precipitate is soluble in excess of the cadmium salt solution and also in boiling water being again precipitated in a crystalline form from the latter on cooling. Zinc and cadmium possibly give rise to the formation of double salts.

The substance does not react with potassium chromate and potassium ferro- or ferri-cyanide solution. From the properties and reactions described above, it is clear that the substance does not give any cobalt ion, cyanide ion or thiosulphate ion in solution. It contains a complex anion containing thiosulphate and cyanogen radicle with cobalt as the central atom. In solution however it slowly hydrolyses into aquo-pentacyano-cobaltiate on warming as it then gives a reddish brown precipitate with silver nitrate solution. This is further confirmed by conductivity measurements. The hydrolysis proceeds thus :—

$$K_4\left[(CN)_5 Co.S_2O_3\right] + H_2O \rightleftharpoons K_3\left[(CN)_5 Co.H_2O\right] + K_2S_2O_3.$$
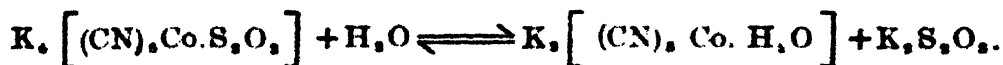
For analysis the substance was decomposed by heating with hot concentrated sulphuric acid ; the solution was diluted and cobalt was precipitated as cobalt sulphide from the solution. The latter was then converted into cobalt sulphate and weighed as such. Potassium was estimated in the filtrate as potassium sulphate. The thiosulphate was estimated by oxidation to sulphate with ammoniacal hydrogen peroxide and then by precipitation as barium sulphate. Cyanogen was converted into ammonium salts by heating with strong sulphuric acid and potassium bisulphate and then distilling the ammonia as usual. (Found : Co, 12·85 ; 13·06 ; S, 13·94 ; N, 15·13 ; K, 33·63. $K_4[S_2O_3Co.(CN)_5]$ requires Co, 12·91 ; S, 14·00 ; N, 15·31 ; K, 34·1 per cent.).

Conductivity Measurements.

Following results were obtained with a freshly prepared solution of the substance in conductivity water at 20°C.

v (dilution)	148·9,	297·8,	595·6,	1191·2
M_v	386·9,	416·2.	488·2,	567·6

A determination at a higher temperature at 26°C gave much higher values which further increased on keeping the solution, specially in contact with the electrodes in the cell—the latter catalytically accelerating the hydrolysis already appreciable at this temperature.

Molecular conductivity for hexammine platinic chloride $[Pt(NH_3)_6]Cl_4$ and potassium ferrocyanide $K_4[Fe(CN)_6]$ which also furnish a tetravalent complex ion (positive in the case of platinum and negative in the case of iron) in addition to four simple monovalent ions are quoted here for comparison. (Weinland, " Einführung in die Chemie der Komplex-Verbindungen," p. 5).

v (dilution) :　　　　128　256　512　1042
M_v for $K_4[Fe(CN)_6]$ at 25°C. 432　477　520　558

M_v for $[Pt(NH_3)_6]Cl_4$ at 25°C 433 485 528
　　　(Werner and Miolati Zeit. physikal. Chem., 1894, **14**, 506.)

Agreement between these values and those obtained for the present substance is sufficiently close to confirm the existence of a tetravalent complex ion in a solution of the latter.

Molecular Weight Determination.

Molecular weight of the substance in aqueous solution was determined by the freezing point method with the following results.

Concentration per 100 gm. of water	Depression.	M. W. found.
2·0560 gm.	0 ·266°	139·1
1·47 gm.	0 ·198°	188·6

These two determinations were made in fairly dilute solutions. Theoretically the molecular weight calculated on the assumption that the salt in solution is completely ionized, should have been 91·4. The higher values therefore indicate that even at this dilution the

substance is not completely dissociated. This in fact holds for all salts with polyvalent ions, the dissociation progressing by stages. In the present case the gradual dissociation of the salt in solution can be represented thus :

$$K_4X \longrightarrow K^{\cdot} + K_3X' \longrightarrow 2K^{\cdot} + K_2X'' \longrightarrow 3K^{\cdot} + KX''' \longrightarrow 4K^{\cdot} + X''''$$

$$\text{where } X = [S_2O_3 \ Co. \ (ON)_6].$$

Apparently the last stage of dissociation was not reached in the present instance. Experiments with further diluted solution were not possible on account of very small depression of the freezing point that would result and vitiate the accuracy of determinations.

Coagulating Power and Absorbability.

A solution having 0·01 mol. per litre was prepared using conductivity water. And its coagulating power was compared against that of a potassium ferrocyanide solution of the same strength upon a positive ferric hydroxide sol with the following results :

One c.c. of the potassium ferrocyanide solution diluted to 2·5 c.c. with water and mixed with 2·5 c.c. of the ferric hydroxide sol coagulated the latter completely in 0·53 secs. Whereas even 0·15 c.c. of the 0·01 M solution of the substance almost instantaneously effected the complete coagulation of the same amount of ferric hydroxide sol under exactly the same conditions. This shows that the coagulating power of the complex negative ion of the substance under examination is much higher than that of the complex ferrocyanide ion with a negative valency of four. The valency of the complex anion of the thiosulphato-compound is therefore likely to be at least as high as that of the ferrocyanide ion (Freundlich, *Koll-Zeit.*, 1922, 31, 243). This is also supported by the charge-reversal effect produced in a ferric hydroxide sol when the latter was mixed with a solution of the substance with a concentration of about 0·02 mol per litre.

Magnetic Susceptibility.—The substance when examined in a Curie's balance was found to be diamagnetic. This is perfectly in agreement with Rosenbohm's results (*Zeit. physikal. Chem.*, 1919, 93, 693) who examined a large number of complex metallic or co-ordination compounds and found that almost all the complex

cobaltic compounds thus examined were diamagnetic. That the substance is a definite co-ordination cómpound is thus 'placed beyond doubt. All the co-ordinated cobalt compounds, as shown by Welo and Baudisch (*Nature*, 1925, **116**, 606), should exhibit diamagnetic susceptiblity due to their having closed electronic configurations resembling that of the inert gas krypton as interpreted by Sidgwick in developing his "effective atomic number" rule (*J. Chem. Soc.*, 1923, **123**, 725).

Action of Sodium Nitrite upon Thiosulphato-pentammine Cobaltic Chloride.

Finely powdered thiosulphato-pentammine cobaltic chloride was digested with warm strong solution of sodium nitrite. The former gradually went into solution with slow evolution of ammonia. The solution after filtration was heated on the water-bath when more ammonia was evolved and a very sparingly soluble yellow product separated out. This was first thoroughly washed with cold water, then with alcohol and finally dried in air.

On analysis and examination, the substance was found to be pure trinitrito-triammine cobalt $[(NO_2)_3Co(NH_3)_3]$. This affords a very easy and rapid method of preparing pure trinitrito-triammine cobalt. (Found: Co, 23·84; NH_3, 20·57. $[(NO_2)_3Co(NH_3)_3]$ requires Co, 23·8; NH_3, 20·56 per cent.).

My best thanks are due to Mr. S. G. Chowdhury for assisting me in determining the charge-reversal of the ferric hydroxide sol and to Mr. H. G. Bhar for testing the magnetic property of the substance.

UNIVERSITY COLLEGE OF SCIENCE,
     CALCUTTA.

Benzidine Rearrangement in the Heterocyclic Series. Part I.

By Prafulla Kumar Bose.

The present investigation was undertaken with the expectation of obtaining 4 : 5-disubstituted aminothiodiazines (I) which will result by the interaction of halogenated ketones with 1-substituted thiosemicarbazides.

When equimolecular quantities of 1-phenylthiosemicarbazide and a halogenated ketone, such as monochloracetone, ω-bromacetophenone or p-methyl-ω-bromacetophenone, were shaken in absolute alcohol at the room temperature, the hydrochloride or hydrobromide of the condensation product was obtained in quantitative yield. The base has the same composition as (I), where $R = C_6H_5$, CH_3, or p-$CH_3 \cdot C_6H_4$. These bases, on acetylation with acetic anhydride, yielded *monoacetyl* derivatives. Moreover, they were found to give colour reactions with concentrated sulphuric acid (*vide* Experimental part).

The above bases, which are formed by the elimination of a molecule of water and a molecule of hydrochloric or hydrobromic acid, may have one of the following structures :

$$\bullet NH_2 \cdot C \underset{S-CH}{\overset{N-NPh}{<\qquad>}} C \cdot R$$

(I).

$$\underset{R \cdot C \quad S}{\overset{N=C \cdot NH \cdot NHPh}{|\quad|}}$$
$$\underset{CH}{\bigvee}$$

(II).

$$NH=C \underset{S-CH}{\overset{NH \cdot NPh}{<\qquad>}} C \cdot R$$

(III).

$$\underset{R \cdot C \quad S}{\overset{NH-C : N \cdot NHPh}{|\quad|}}$$
$$\underset{CH}{\bigvee}$$

(IV).

$$\underset{S \quad C \cdot R}{\overset{NH=C-N \cdot NHPh}{|\quad|}}$$
$$\underset{CH}{\bigvee}$$
(V).

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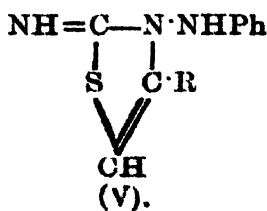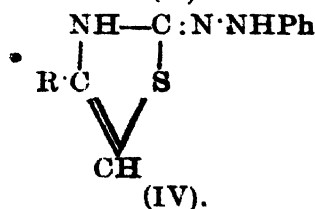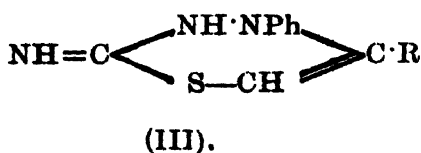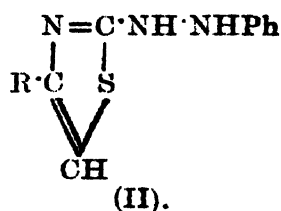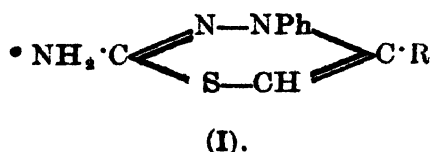
Of these the last three contain either an imino or a hydrazino group. It was, therefore, considered desirable to study the action of aqueous hydrochloric acid on the condensation products. These would be hydrolysed to ammonia or phenyl hydrazine in case they possessed any of the last three structures (III, IV, V), thus:

$$NH=C \overset{NH \cdot NPh}{\underset{S-CH}{<}} C \cdot R \xrightarrow[\text{[HCl]}]{H_2O} OC \overset{NH \cdot NPh}{\underset{S-CH}{<}} C \cdot R + NH_3$$

(III).   (VI).

$$\underset{\underset{CH}{\overset{\|}{V}}}{\overset{NH-C=N \cdot NHPh}{R \cdot C \qquad S}} \xrightarrow[\text{[HCl]}]{H_2O} \underset{\underset{CH}{\overset{\|}{V}}}{\overset{NH-CO}{R \cdot C \qquad S}} + NH_2 \cdot NHPh$$

(IV).   (VII).

$$\underset{\underset{CH}{\overset{\|}{V}}}{\overset{NH=C-N \cdot NHPh}{S \qquad C \cdot R}} \xrightarrow[\text{[HCl]}]{H_2O} \underset{\underset{CH}{\overset{\|}{V}}}{\overset{OC-N \cdot NHPh}{S \qquad C \cdot R}} + NH_3$$

(V).   (VIII).
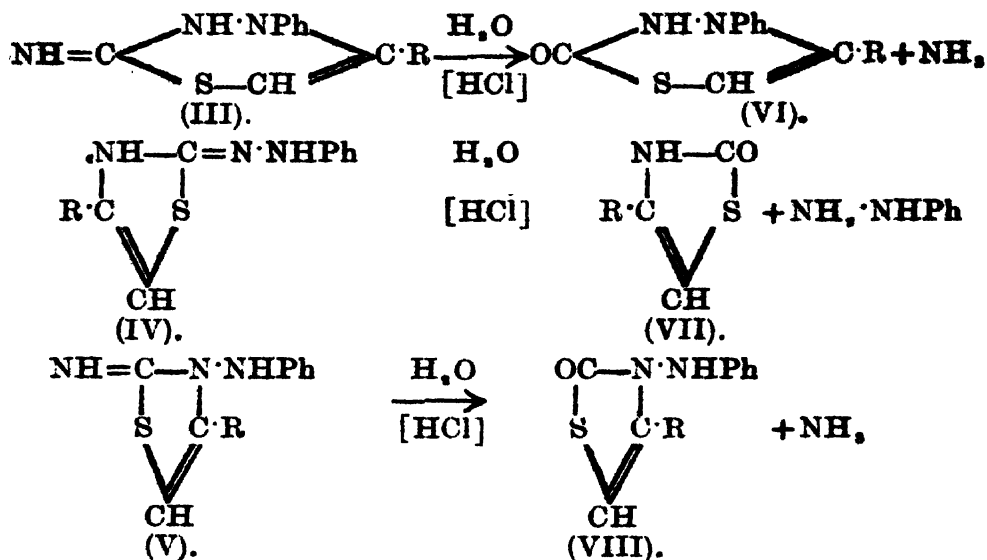
Accordingly each of the bases was boiled with dilute hydrochloric acid for 5-15 minutes. The products were almost quantitatively converted into isomeric bases by the influence of this reagent. These (isomeric bases) dissolved in concentrated sulphuric acid without developing any colour and yielded, on acetylation with acetic anhydride, *diacetyl* derivatives, and were found to be diacid bases, the chloroplatinates having the composition, B,H_2PtCl_6. These results are not consistent with any of the formulae (I), (III), (IV) or (V), some of which can explain the isomeric change in a satisfactory manner but fail to account for the general chemical properties.

On the assumption that the bases have the structure (II), the isomeric transformation brought about by hydrochloric acid may be regarded as an instance of benzidine rearrangement.

$$\underset{\underset{CH}{R \cdot C}}{\overset{C-NH \cdot NH}{\underset{\|}{N}}} \bigcirc S \longrightarrow \underset{R \cdot C}{\overset{C \cdot NH_2}{\underset{\|}{N}}} \underset{C}{\overset{}{\longrightarrow}} \bigcirc NH_2$$

(II).   (IX).
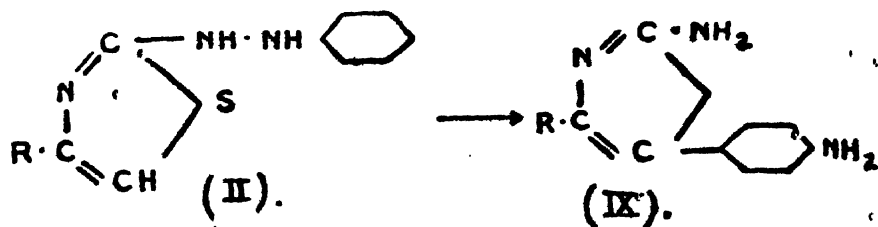
A very similar case has been placed on record by Fargher and Pyman (*J. Chem. Soc..* 1919, **115**, 222; *cf.* also Pyman and Ravald, *ibid*, 1920, **117**, 1426) who found that in the reduction of 2-benzene-azoglyoxaline (X) with stannous chloride and hydrochloric acid, the main product was 2-amino-4-*p*-aminophenylglyoxaline (XII), the rearrangement obviously taking place through the intermediate hydrazo compound (XI).

(X).   (XI).   (XII).
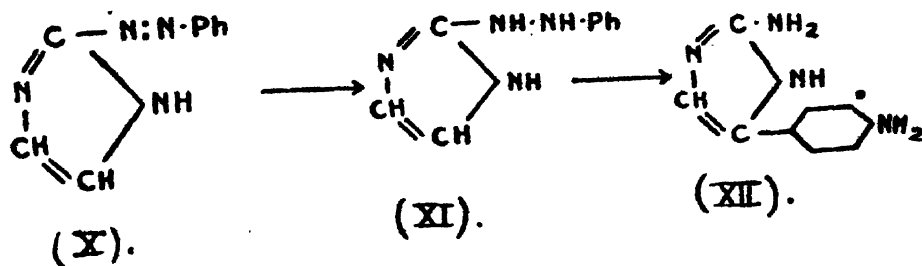
According to these investigators (*loc. cit.*) "the occurence of a rearrangement of the benzidine type in a five-membered heterocyclic nucleus seems remarkable at first sight, but a closer inspection of the formula shows that the conjugated system connecting the 2- and 5-carbon atoms of the glyoxaline ring is similar to that existing in the benzene nucleus."

In the present instance the five-membered heterocyclic ring happens to be a thiazole of which the 2- and 5-carbon atoms are connected by a conjugated system exactly similar to that present in the glyoxaline ring mentioned above. It is, moreover, a hydrazo compound and indeed a benzidine rearrangement is to be expected. The formula (IX) for the isomeric bases easily explains the formation of diacetyl derivatives. A direct and more conclusive evidence has been furnished by the formation of *p*-acetyl-aminobenzoic acid on oxidation of the diacetyl compound of formula IX (R$=$CH$_3$) by acid permanganate solution. This result also eliminates the possibility that the bases had undergone semidine rearrangement yielding compounds of the type (XIII) or (XIV).

(XIII).   (XIV).
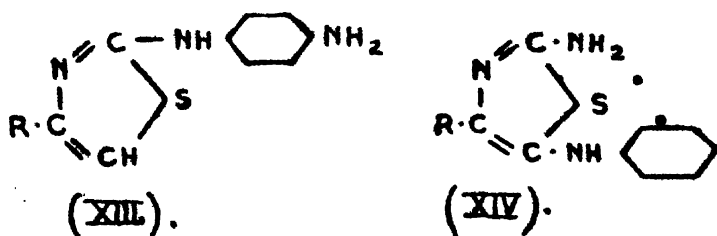
EXPERIMENTAL.

2-Phenylhydrazino-4-phenyl-1:3-thiazole : *Formula* II (R=C₆H₅).
—Finely powdered 1-phenylthiosemicarbazide (1·7 g.) and ω-brom-
acetophenone (2 g.) were shaken with absolute alcohol (15 c.c.)
without the application of heat. The components gradually dis-
solved and the solution became warm. After a few minutes crys-
tals separated out. Ether (20 c.c.) was added to the product and
the greenish white crystals were collected, washed with ether and
dried (3·4 g.). The *hydrobromide* was dissolved in a mixture of
warm pyridine and alcohol, and diluted with water. The colour-
less needles of the base, which separated out, were twice recrystal-
lised from dilute acetone ; m.p. 191°. (Found : C, 67·30; H, 5·00.
$C_{15}H_{13}N_3S$ requires C, 67·42; H, 4·87 per cent.).

It gave a bluish green colour with concentrated sulphuric acid;
the colour vanished on dilution. It is soluble in cold acetone, hot
benzene or pyridine, and only sparingly so in ether or alcohol.

The *acetyl* derivative was twice crystallised from alcohol in
glistening transparent needles, m. p. 161°. (Found : N, 13·56.
$C_{17}H_{15}ON_3S$ requires N, 13·59 per cent.).

Action of Hydrochloric Acid on the above Base : *Formation of*
2-Amino-4-phenyl-5-p-aminophenyl-1 :3-thiazole.

The base (1 g.) was boiled during 10 minutes with 100 c.c.
of 2·5N—hydrochloric acid. The solution was cooled, filtered and
the filtrate was made alkaline with ammonia. An oil separated out
which hardened in the course of a few hours. This was removed,
washed with cold water and dried (0·85 g.). It was crystallised
from dilute alcohol using animal charcoal as a decoloriser. Pale
yellow rectangular plates, m.p. 193-4°, were obtained. (Found :
C, 67·34; H, 5·54; S, 11·73. $C_{15}H_{13}N_3S$ requires C, 67·42; H,
4·87; S, 11·98 per cent.).

It does not give any color reaction with concentrated sulphuric
acid. This base is also obtained if the condensation between the
thiosemicarbazide and the bromoketone is carried out in boiling
alcoholic solution for about 10 minutes. It is easily soluble in
alcohol, benzene, acetone, chloroform and pyridine, sparingly in
ether and ligroin.

The *hydrochloride* crystallises from dilute hydrochloric acid in colorless needles. It decomposed above 260°. (Found : Cl, 20·18. $C_{18}H_{13}N_3S$, 2HCl, H_2O requires Cl, 19·83 per cent.).

The *picrate* formed yellow rectangular plates, m.p. 1:4-85° d.

The *chloroplatinate* formed yellow microscopic crystals which had no m.p. (Found : Pt, 28·6⁻. $C_{18}H_{13}N_3S$, H_2PtCl_6 requires Pt, 28·80 per cent.).

2-*Acetylamino-4-phenyl-5-p-acetylaminophenyl-1 : 3-thiazole*.

On adding acetic anhydride to the base the latter dissolved with evolution of considerable heat. On boiling the solution for a short time, a crystalline product separated out. The whole was allowed to cool, the solid was collected, washed with alcohol, and crystallised from a mixture of pyridine and dilute alcohol as long, white needles, m. p. 285°. These, however, changed into transparent, pale brown, compact prisms, m. p. 285-86°, on keeping for a few days in contact with its mother-liquor. (Found : N, 12·06. $C_{19}H_{17}O_2N_3S$ requires N, 11·97 per cent.).

2-*Phenylhydrazino-4-p-tolyl-1 : 3-thiazole : Formula* II(R=p-C_7H_7).

1-Phenylthiosemicarbazide (3·4 g.) and *p*-methyl-ω-bromacetophenone (4·2 g.) were shaken with absolute alcohol (25 c. c.) in a flask. These went into solution with rise of temperature and colorless needles began to separate out almost immediately. The flask was cooled and ether (75 c. c.) was added. The *hydrobromide* of the condensation product was filtered off, washed with ether and dried. The yield was quantitative. The base, 2-phenylhydrazino-4-*p*-tolyl-1 : 3-thiazole was liberated using pyridine. When crystallised from a mixture of pyridine and alcohol, it formed long, colorless needles, m. p. 186°. (Found : N, 15·02. $C_{16}H_{15}N_3S$ requires N, 14·95 per cent.).

It is easily soluble in acetone, pyridine, or ether but sparingly in alcohol. It gave a deep green coloration with concentrated sulphuric acid.

The *acetyl* derivative, obtained by heating the base with acetic anhydride, crystallised from alcohol in colourless, soft star-like aggregates, melting at 146°. (Found : N, 13·12. $C_{18}H_{17}ON_3S$ requires N, 13·00 per cent.).

Action of Hydrochloric Acid on the above Base : Formation, of 2-Amino-4-p-tolyl-5-p-aminophenyl-1 : 3-thiazole.

The base (1·5 g.) was boiled with 100 c. c. of 2·5N-hydrochloric acid for about 15 minutes. The yield of the isomeride amounted to 1·4 g. It is easily soluble in methyl or ethyl alcohol, pyridine, acetone or ether. It separated from dilute alcohol in pale brown needles melting at 182°. (Found: N, 14·82. $C_{16}H_{15}N_3S$ requires N, 14·95 per cent.). It gave only a very faint yellowish green color with concentrated sulphuric acid.

The diacetyl derivative, namely 2-*acetylamino-4-p-tolyl-5-p-acetylaminophenyl*-1 : 3-*thiazole* crystallised from glacial acetic acid in white, slender needles, m. p. 290°. (Found: N, 11·44. $C_{20}H_{19}O N_3S$ requires N, 11·51 per cent.).

The *hydrochloride* crystallised from dilute hydrochloric acid in long, colorless needles. (Found: Cl, 19·92. $C_{16}H_{15}N_3S$, 2HCl requires Cl, 20·06 per cent.).

The *chloroplatinate* was obtained in yellow microscopic crystals, which had no m. p. (Found: Pt, 27·34. $C_{16}H_{15}N_3S$, H_2PtCl_6, H_2O requires Pt, 27·51 per cent.).

The *picrate* crystallised in yellow microscopic crystals, m. p. 215° (with previous sintering and decomposition).

2-*Phenylhydrazino-4-methyl*-1 : 3-*thiazole* : *Formula* II $(R=CH_3)$.

1-Phenylthiosemicarbazide (3·2 g.) and monochloracetone (2 g.) were shaken with 25 c. c. of absolute alcohol, till the former had completely dissolved. The solution was allowed to stand for a few minutes, and treated with pyridine (7 c.c.) and water (50 c.c.). The needle-shaped crystals, which separated out, were collected, washed with water, and recrystallised from a mixture of pyridine and alcohol in colorless rectangular plates, m.p. 179°. (Found: C, 58·88; H, 5·62. $C_{10}H_{11}N_3S$ requires C, 58·53; H, 5·30 per cent.).

2-Phenylhydrazino-4-methyl-1 : 3-thiazole is easily soluble in benzene or acetone but almost insoluble in ligroin. It imparted a rose-red coloration to concentrated sulphuric acid. The substance turned brownish red on keeping for days or on heating above 150°.

The *acetyl* derivative formed colorless shining needles or plates, m. p. 232°. (Found: N, 17·03. $C_{12}H_{13}ON_3S$ requires N, 17·00 per cent.).

It is easily soluble in benzene, ether, chloroform or dilute hydrochloric acid, but sparingly in benzine.

Action of Hydrochloric Acid on the above Base: *Formation of 2-Amino-4-methyl-5-p-aminophenyl-1 : 3-thiazole.*

The base (1·2 g.) was boiled with normal hydrochloric acid (25 c.c.) for about 5 minutes. Shining plates were obtained on making the cold solution alkaline with caustic soda. The dried material (1 g.) was twice recrystallised from dilute methyl alcohol using animal charcoal. It forms pale-brown shining plates, m. p. 181°. (Found : N, 20·34. $C_{10}H_{11}N_3S$ requires N, 20·48 per cent.).

It is easily soluble in alcohol or pyridine but sparingly in benzene or chloroform. It did not respond to the color reaction characteristic of its isomeride.

The *hydrochloride* crystallised from concentrated hydrochloric acid solution in long, silky needles which decomposed above 240°. It contains 2 molecules of water of crystallisation. (Found : Cl, 22·59. $C_{10}H_{11}N_3S, 2HCl, 2H_2O$ requires Cl, 22·62 per cent.). On drying in a steam-oven only $1\frac{1}{4}$ molecules of water could be driven off. (Found : Cl, 24·56. $C_{10}H_{11}N_3S, 2HCl, \frac{1}{4}H_2O$ requires Cl, 24·74 per cent.).

The *chloroplatinate* was obtained as small, orange pointed needles. (Found : Pt, 30·82. $C_{10}H_{11}N_3S, H_2PtCl_6, H_2O$ requires Pt, 30·80 per cent.).

The *picrate* formed yellow, star-like aggregates, m. p. 214° (with decomp.)

Benzylidene Derivative.—To a hydrochloric acid solution of the base, benzaldehyde was added drop by drop and shaken when a deep yellow crystalline precipitate immediately separated out. This was collected, washed with dilute hydrochloric acid and dried. The product (hydrochloride of the monobenzylidene derivative) was then dissolved in pyridine and the base precipitated by water. From dilute methyl alcohol it separated in yellow needles, m. p. 177°. (Found : N, 14·82. $C_{17}H_{15}N_3S$ requires N, 14·38 per cent.).

The *diacetyl* derivative, *2-acetylamino-4-methyl-5-p-acetylaminophenyl-1 : 3-thiazole* was obtained from dilute pyridine in long colorless needles, which gradually changed into hard prismatic crystals, m. p. 292°, on being kept in contact with the mother-liquor for several days. (Found : N, 14·65. $C_{14}H_{15}O_2N_3S$ requires N, 14·53 per cent.).

Oxidation of 2-Acetylamino-4-methyl-5-p-acetylaminophenyl-1:3-thiazole.

The acetyl derivative (2 g.) was dissolved in acetone (150 c.c.) nd to it dilute sulphuric acid (125 c. c. of 20 per cent.) was added when the substances was precipitated in a fine state of division. A 2% solution of potassium permanganate was gradually dropped in with constant shaking at the ordinary temperature when the acetyl derivative gradually went into solution. The addition of permanganate was stopped when the pink color persisted for a few seconds, about 135 c. c. being required. The solution was then just made alkaline with a concentrated solution of sodium carbonate and filtered. The filtrate was concentrated on the water-bath till crystals of sodium sulphate began to separate. It was then filtered off and the filtrate acidified with concentrated hydrochloric acid when a white precipitate of p-acetylaminobenzoic acid was obtained. This was collected, washed with a little cold water and dried (0·8 g.). On crystallisation from water (using animal charcoal), it formed long glistening plates, m. p. 255-56°. The m.p. of this substance when mixed with a pure specimen of p-acetylaminobenzoic acid remained unchanged. The identity was further established by a nitrogen estimation. (Found: N, 8·01. $C_9H_9O_3N$ requires N,.7·82 per cent.).

Synthesis of Substituted Ureas and Thio-ureas.

By Ramani Mohan Roy and Jñanendra Nath Ray.

Weith (*Ber.*, 1876, **9**, 820) and all other workers after him obtained sym-di-derivatives by heating together urea and the amines at 170° or above, the only experience to the contrary being that of Fleicher (*Ber.*, 1879, **9**, 995) who obtained mono-phenyl urea from urea and aniline. Our object was to establish the condition under which *mono*-substituted products would be produced in good yield.

It is now recognised that in the case of urea all the reactions indicated below are *reversible* (*cf.* Davis and Underwood, *J. Amer. Chem. Soc.*, 1922, **44**, 2595).

1. $NH_4N:CO \rightleftharpoons NH_3 + HN:CO \rightleftharpoons NH_2.CO.NH_2$
2. $HN:CO + NH_2R \rightleftharpoons NH_2 \cdot CO \cdot NHR \rightleftharpoons NH_3 + RN:CO$
3. $RN:CO + NH_2R \rightleftharpoons RNH.CO.NHR.$

The reaction between urea and the amines is thus primarily dependent on the "urea dearrangement" (equation 1). Phosphoric oxide was chosen as the condensing agent as it was expected that it would accelerate the dearrangement by removing the ammonia from the zone of action. This expectation was amply realised; for in the presence of phosphoric oxide reaction took place at temperatures as low as 105—115°, and 66 to 88 per cent. of the urea was converted.

Disubstituted ureas are formed by the breaking up of the mono-derivative into the corresponding *iso*cyanate. Davis and Underwood ((*loc. cit.*) showed that mono-phenyl urea breaks up in this way at 168°. The low temperature used in our experiments explains why the mono-derivatives were produced in good yield. This desideratum was further achieved by using an excess of urea, so that very little of the amine was available for the third reaction.

When the investigation was extended to thio-urea, a higher temperature (170°) was found necessary and considerable hydrogen sulphide was given off during the process. *o*-Toluidine and *p*-toluidine gave *mono*-substituted thio-ureas, while *m*-toluidine did not give any thio-urea derivative at all. This shows that *at the temperature of the experiment* thio-urea has the diamide structure and that the equations are similar to those in the case of urea.

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By heating thio-urea and aniline in the presence of phosphoric oxide a small amount of mono-phenyl urea was obtained. The thio-urea undoubtedly acted partially in its ψ-form, yielding phenyl-guanidine, which broke up into ammonia and phenylurea. It might be interesting to recall in this connection the work of Hans Krall (*J. Chem. Soc.*, 1915, **107**, 1397) who maintains that guanidine decomposes into carbon dioxide and ammonia, and not into urea and ammonia. Obviously this is not so in the case of phenylguanidine.

When urethane and aniline were refluxed with phosphoric oxide in xylene solution, diphenyl urea was obtained exclusively and in good yield. Thio-urethane also acted in the same way. The urethane probably breaks up into alcohol and *iso*cyanic acid thus :

$$NH_2COOEt \rightleftharpoons HN:CO + EtOH,$$

and the latter reacts with aniline according to reactions 2 and 3 already formulated. Here the phosphoric oxide accelerates the 'dearrangement' of the monophenyl urea first formed into phenyl *iso*cyanate and this explains why the di-derivative is formed to the exclusion of the mono-substituted product. It remains to refer to the preparation of di-butyl urea by Dixon (*J. Chem. Soc.*, 1895, **67**, 556) who obtained it by heating together butylamine and urethane at a temperature as high as 220°.

<center>EXPERIMENTAL.</center>

Aniline and Urea.—Urea (4 g.) and aniline (5 c. c.) were heated together with phosphoric oxide (2 g.) at 110° for 2 hours. The mass was cooled, washed first with water and then with benzene, and recrystallised from alcohol when fine needles of mono-phenyl urea, m. p. 146°, were obtained (yield 2·5 g.).[1] (Found : N, 20·7. $C_7H_8N_2O$ requires N, 20·5 per cent). On recrystallising from acetone a condensation product, m. p. 222·5°, was obtained. (Found : N, 15·45. $C_{10}H_{14}NO$ requires N, 15·9 per cent.).

ο-*Toluidine and Urea.*[2]—These were heated together in molecular proportions in presence of the requisite amount of phosphoric oxide at 115-20° for 2 hours. The product was purified as before and recrystallised from absolute alcohol ; m. p. 182-3°. (Found ; N, 18·8. $C_8H_{10}N_2O$ requires N, 18·7 per cent.).

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[1] Fleicher (*loc. cit.*) obtained mono-phenyl urea by heating aniline and urea at 150-170°. Weith (*loc. cit.*) and Baeyer (*Annalen*, 1864, **131**, 252) obtained the di-derivative at 160-190°. Davis and Underwood obtained both mono- and di-derivatives.

[2] Davis and Underwood obtained o-tolyl urea by heating at 160° for 7 hours.

m-Toluidine and Urea.[a]—*m*-Toluidine (7 c.c.), urea (10 g., nearly 4 equivalents) and phosphoric oxide (8 g.) were heated at 120-125° for 4 hours. The product was cooled, washed with cold water and then extracted with boiling water. From the filtrate on keeping overnight 1·5 g. of *m*-tolylurea separated out ; m. p. 141·4° (crystallised from absolute alcohol). Reported m. p. 142°. Mixed m. p. with urea 112°.

The insoluble residue was crystallised from rectified spirit ; yield 4 gms. M. p. 225°. (Found : N, 11·5. $C_{15}H_{16}N_2O$ requires N, 11·7 per cent.). Thus in this experiment 65-70% of the urea was converted. *m*-Toluidine (8 c. c.) urea (5 g., in equivalent amounts) and phosphoric oxide (2·5 g.) were heated at 115° for 2 hours. Only the di-derivative was obtained. The same amounts when heated at 105° for 1½ hours, gave, in addition to the diderivative, a solid, m.p. 125° (crystallised from absolute alcohol). This has not been identified, and the yield was very poor.

p-*Toluidine and Urea.*[a]—Toluidine (4 g.), urea (3 g.) and phosphoric oxide (2-8 g.) were heated at 110-115° for 3 hours. Cooled and washed thoroughly with cold water. The residue was repeatedly extracted with the minimum amount of absolute alcohol. From these alcoholic extracts *p*-tolyl urea (2 g.), m.p. 173-4°, was isolated. (Found : N, 18·3. Calc. N, 18·6 per cent.).

The portion insoluble in alcohol was recrystallised from glacial acetic acid (in which it is very sparingly soluble), when di-*p*-tolyl urea (2·7 g.), m.p. 252°, was obtained. Melting points reported in literature are 244°, 256° and 268°. (Found : N, 11·4. Calc. N, 11·7 per cent.).

Phenetidine and Urea.—Phenetidine (4 g.) was heated with the equivalent amounts of urea and phosphoric oxide at 120° for 4 hours. The product was washed with ice-cold water (slightly acidified) and extracted with very dilute alcohol. The filtrate was concentrated and *p*-ethoxy-phenyl urea or dulcin (1·9 g.) separated out. Crystallised from water and obtained as fine needless ; m. p. 159-61°.

The insoluble residue was crystallised from glacial acetic acid and 2·5 gms. of sym-di-ethoxy-phenyl urea, m. p. 220-28°, were obtained.

Urethane and Aniline.—Equivalent quantities of urethane and aniline were refluxed with phosphoric oxide in xylene solution at 140-5° for 2 hours. The xylene was then distilled off, and the residue

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[a] No reference in the literature. It is obvious that *m*-toluidine does not react in the absence of a condensing agent, and that the monosubstituted product is not obtained unless the urea is in excess.

[a] Davis and underwood obtained the di-derivative at 160°.

washed with acidulated water. The crude residue melted at 244.5° and was therefore practically pure diphenylurea. On crystallising from absolute alcohol the m.p. rose to 245-6°.

Thio-urea and Aniline.—Thio-urea (4 g.) aniline (5 c. c.) and phosphoric oxide (2·3 g.) were heated at 140° for 3 hours when hydrogen sulphide was evolved. The mass was cooled and extracted with water, and the aqueous solution concentrated. Fine radiating needles separated out of the solution. This was crystallised from 50 per cent spirit ; m.p. 145°-6°. This was identified to be mono-phenyl urea by a mixed m.p. with a sample prepared from aniline and urea.

The portion insoluble in water was crystallised repeatedly from rectified spirit, but a pure product could not be isolated. The substance melted at 125-35°. (Found : N, 13·65 per cent.). It also contains sulphur and phosphorus and was not identified.

o-Toluidine and Thio-urea.—Heated at 170° for 4 hours. Extracted with water and from the filtrate a compound, m.p. 90-32°, was isolated. This has not been identified, but seems to be a urea derivative. It does not contain sulphur.

The insoluble oily layer was induced to crystallise and o-tolyl-thio-urea was obtained. Crystallised from dilute spirit ; m.p. 160°. (Found : N, 17·46. Calc. N 16·9 per cent.).

p-Toluidine and Thio-urea.—The usual procedure was followed but there was no evolution of H_2S. No definite compound could be isolated from the aqueous extract of the reaction product. The insoluble matter was crystallised several times from absolute alcohol m. p. 172°. Recorded m. p. of p-toly thiourea is 188° (182° ?) and that of the di-p-tolyl compound, 176°. The analysis, however, proved it to be p-tolyl thiourea. (Found : N, 16·88. Calc. N 16·87 per cent.).

Thio-urethane and Aniline—Thio-urethane was prepared by passing NH_3 into an alcoholic solution of potassium hydroxide and carbon disulphide. The product was triturated with sufficient warm water and the substance crystallised from alcohol when shining white feathery crystals of diphenyl thiourea, m.p. 148°, were obtained. Reported m.p. 153°.

This work was carried out in 1922-23.

Photochemical Oxidation of Leuco-Malachite Green by means of Uranyl Nitrate in Monochloracetic Acid Solution.

By

Jnanendra Chandra Ghosh and Jadulal Mukherjee.

The photochemical oxidation of some leuco-bases has been recently studied from the standpoint of technical application in colour photography by Carroll (*J. Phys. Chem.*, 1926, **30**, 130). His paper may be referred to for previous work in this subject. Carroll finds that the photochemical oxidation of the leuco-bases offers little hope of utility as a photographic process but it may be followed by optical methods of analysis and is well adapted to study of photochemical catalysis.

In the present paper we have studied the photochemical oxidation of leuco malachite green by means of uranyl nitrate. The results obtained are important in the sense that certain very simple relations have been discovered between the intensity of illumination, the concentration of the photochemical oxidising agent, and the concentration of the acceptor leucobase.

EXPERIMENTAL.

Leucobase of malachite green was prepared by condensing di-methyl aniline and benzaldehyde in presence of zinc chloride (Fischer, *Annalen*, 1883, **217**, 280, 262). It was purified by several crystallisations. The purified base was dissolved in 10 per cent. aqueous solution of mono-chloracetic acid. Mono-chloracetic acid solution of the base if allowed to stand for a sufficient length of time becomes gradually coloured. Hence each solution

was used for two or three days after it had been prepared. Crystallised uranyl nitrate was dissolved in distilled water and used.

The source of light was a 100 c. p. Pointolite lamp, the strength of the current and voltage of which was maintained constant by means of a regulating resistance. A parallel beam of light was obtained by placing a lens at its focal distance from the point source. Monochromatic light filters as prescribed by Plotnikow (''Lehrbuch der Photochemie'', p. 56, Table 14) were used. The reaction cell was mad by cutting out 1 cm. sq. surface from a piece of brass plate 1 cm. thick and 4 cm. sq. which was afterwards electroplated with ·gold. The solution was kept in the hollow space in this brass plate by means of two optically plane glass plates held fast to the metal plate by means of rubber garters. The reaction cell was placed inside a double walled metal box provided with windows on opposite sides. The metal box was hinged on vertical supports fixed into the observation table of a König Marten spectrophotometer, so that at the time of taking readings the box could be turned through 90° degrees and at that position one half of the slit of the spectrophotometer was illuminated by light passing through the glass plates alone and the other half by light passing through the glass plates and the solution. Through the annular space of the box, water from a thermostat was circulated by means of a pump worked by an electric motor. The temperature within the box was maintained constant within 0·1°C (see Fig. 1).

Spectrophotometer readings were taken with different concentrations of the dye in a given uranyl nitrate solution. By plotting those readings against the concentrations, standard curves were prepared from which concentration of the dye in an unknown solution can be obtained by intrapolation. It has been found that for different uranyl nitrate concentrations with the same concentration of the dye different readings were obtained. Hence three different standard curves were prepared, as shown in Fig. 2, (1) with M/2 uranyl nitrate, (2) M uranyl nitrate, (3) M/4 uranyl nitrate. The concentration of the dye formed during the progress of reaction was obtained by taking the readings at different intervals and calculating from the standard curve. The intensities of the incident light were measured by noting the deflections of a Moll galvanometer connected with a Moll thermopile placed in front of the reaction cell. The galvanometer and the thermopile were calibrated by a Hefner lamp which according to Gerlach, gives on a sq. cm. at a distance

Fig. 1.

A—the position of the reaction cell when it was exposed to the incident light.

B—when the reaction chamber was turned through 90° and spectro-photometer readings were taken.

s—the slit; *a*—the light filters; *c*—the reaction cell; *d*—the glass plates; the blackened portion—the brass plate.
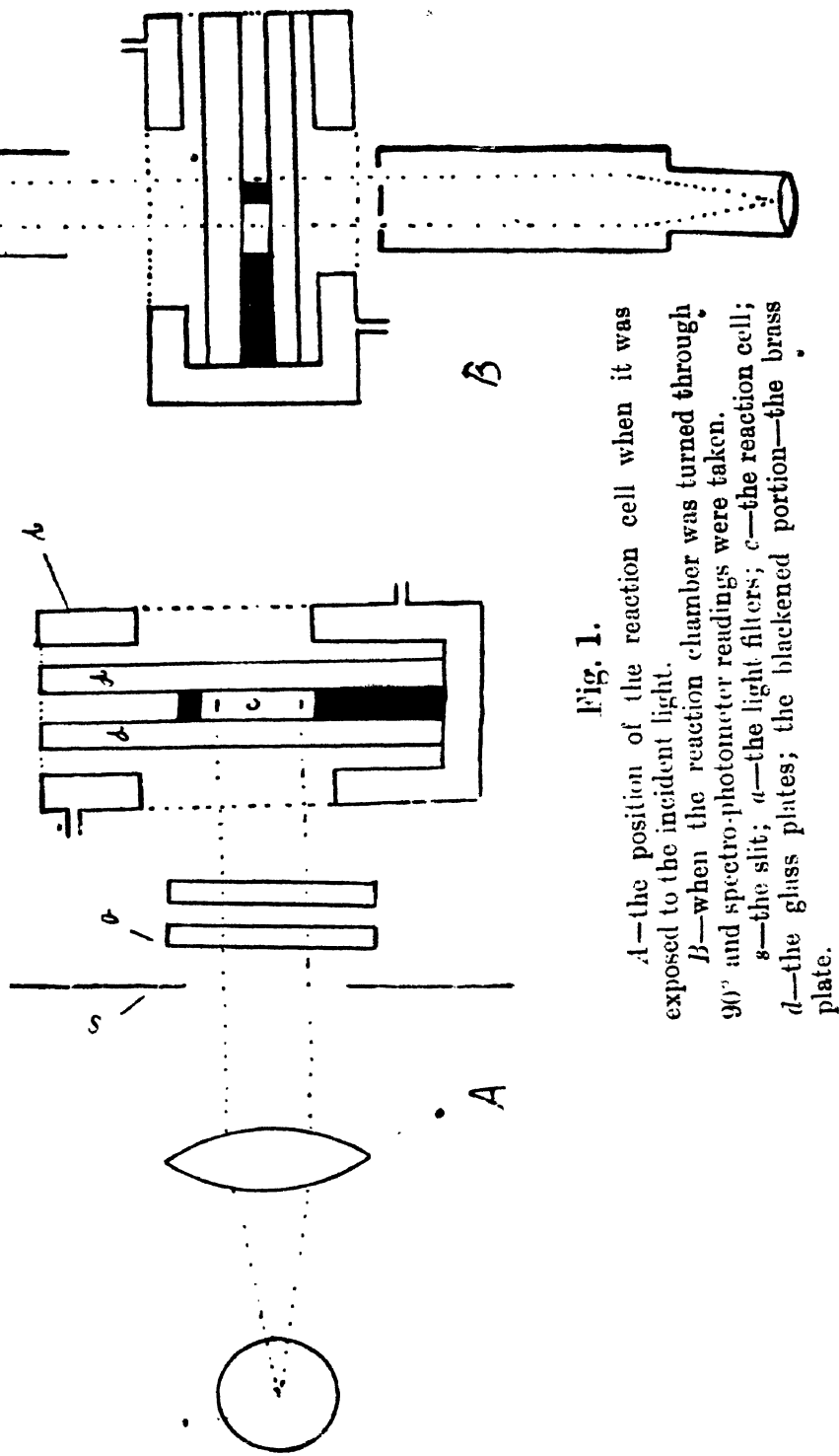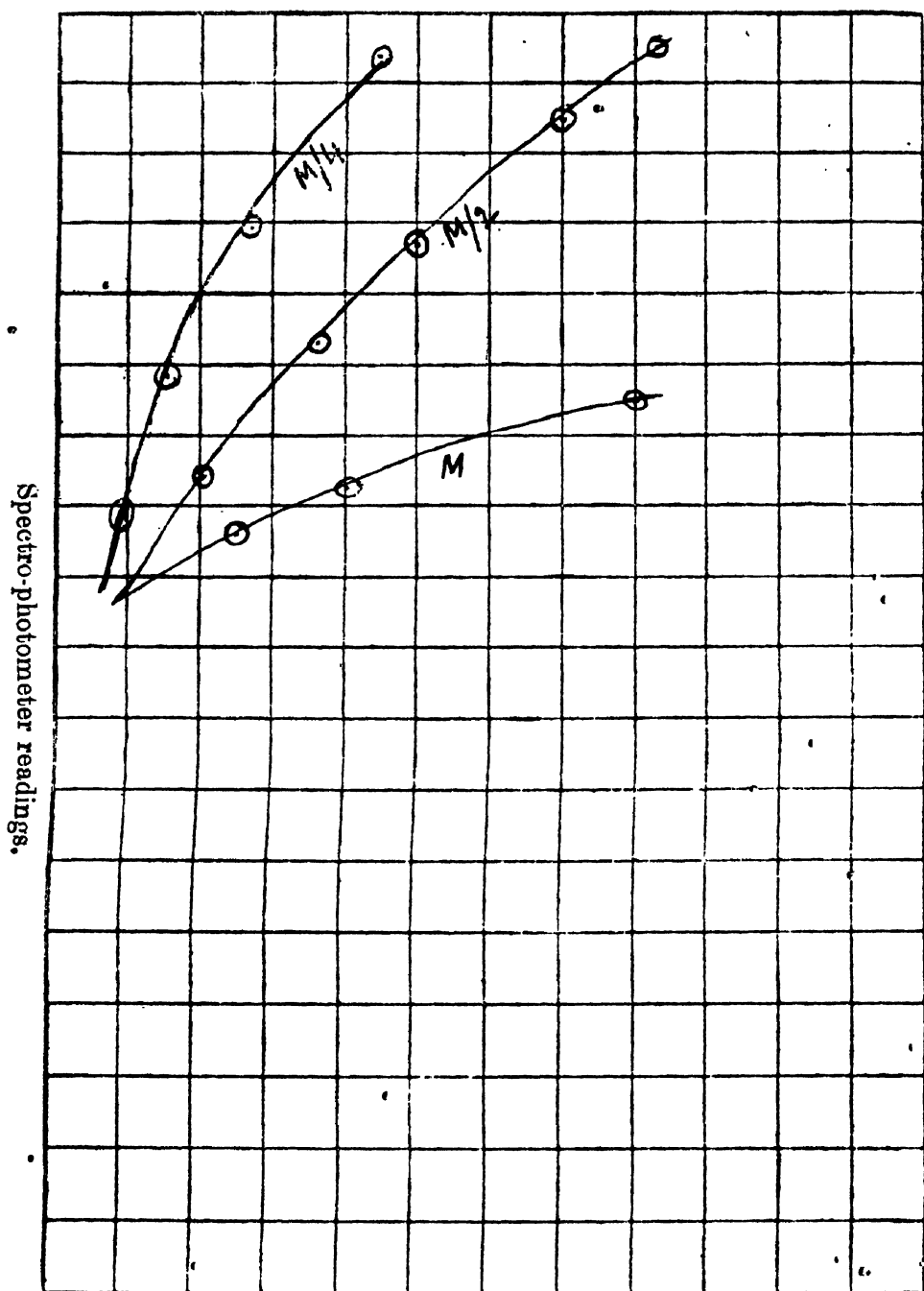
Fig. 2.

Concentration of the dye formed.

of one meter 900 ergs. of radiation. The amount of light absorbed was calculated from the value of extinction coefficient of uranyl nitrate measured with the spectrophotometer.

$$\text{Wave-length} = 440\mu\mu.$$

Reading of the spectro-photo-meter with water in the path of light.	Reading of the spectro-photo-meter with M/2 uranyl nitrate in the path of light.
46	42·1

Length of the cell = 1 mm.

$$\epsilon = \frac{1}{cd} . \log\frac{\tan a_1}{\tan a_2} = 1\cdot 15.$$

The dark reaction.—The velocity of the dark reaction at temperatures below 40°C was found to be too small to be taken into account in studying the velocity and the mechanism of the photo-chemical reaction. No after effect could also be noticed.

Table 1 gives the data for the progress of a given reaction.

TABLE I.

Intensity of the incident light=199 ergs per sq. cm. p. s. Wave-length of the incident radiation=478-410 $\mu\mu$. (Dunkel Blau, Plotnikow, " Lehrbuch der Photochemie," p. 56, Table 14).

Temp. 32°C.

$C_{\text{uranyl nitrate}} = M/2$ $C_{\text{leuco base}} = M/20$

t in minutes.	Conc. of the dye formed.	Rate per hour.
0	0	...
40	0·000046	...
70	0·000056	0·000020
100	0·000066	0·000020
160	0·000084	0·000018
220	0·000104	0·000020
280	0·000124	0·000020

Mean rate per hour = ·000020.

In the above table it will be seen that in the first 40 minutes the reaction rate is distinctly greater than what it is afterwards. The same phenomenon of a period of acceleration has been found also in all the other experiments. This is probably due to the fact that the leucobase at the beginning of the experiment is oxidised by the oxygen dissolved in the solution, the molecules of uranyl nitrate acting as a photosensitiser for this oxidation by oxygen.

The reaction rate is zero molecular and is very slow. The reaction has been found to be zero molecular in all the experiments. In the subsequent tables only the reaction rate and the conditions under which they have been obtained will be given. Table II gives the reaction rate for various intensities of light.

TABLE II.

Temp. 32°C

Wave-length of the incident radiation = 478 — 410 $\mu\mu$

$C_{uranyl\ nitrate} = M/2$	$C_{leuco\ base} = M/20$
Reaction rate	Intensity of light (ergs).
0·000042	400
0·000020	199
0·000007	67
$C_{uranyl\ nitrate} = M/2$	$C_{leuco\ base} = M/10$
Reaction rate	Intensity of light (ergs).
0·000050	400
0·000026	199
0·000008	67

TABLE III.

Intensity of light = 400 ergs. per sq. cm. p. s.

Wave-length = 478—410 $\mu\mu$. Temp. 32°C.

$C_{\text{uranyl nitrate}} = M/2$

Reaction rate	0·000050	0·000042	0·000024	0·000018
$C_{\text{leuco base}}$	M/10	M/20	M/40	M/60

Intensity of light = 199 ergs.   Wave-length = 478-410 $\mu\mu$

$C_{\text{uranyl nitrate}} = M/2$

Reaction rate	0·000026	0·000020	0·000012
$C_{\text{leuco base}}$	M/10	M/20	M/40

TABLE IV.

Intensity of light = 400 egrs.   Wave-length = 478—410 $\mu\mu$

$C_{\text{leuco base}} = M/20$ Temp. 32°C

Reaction rate	0·000042	0·000086	0·000020
$C_{\text{uranyl nitrate}}$	M/2	M	M/4

Discussion.

In our reaction there are two substances which react together and bring about a photochemical change. Uranyl nitrate which is coloured yellow has got absorption band in the visible region, while the leuco-base solution which is perfectly colourless is not sensitive to radiation in the visible region. According to the newer theories of the mechanism of a photochemical reaction active molecules of the photoactive components are first produced by absorption of radiant energy. The concentration of the active molecules formed is given by the equation

$$k I_0 \left(1 - e^{-\epsilon c l}\right) \qquad \ldots \qquad \ldots \qquad \text{Eq. 1}$$

where I_0 is the intensity of the incident light, ϵ the molecule extinction coefficient, c the concentration of the photoactive molecule, l the thickness of the solution and k a constant.

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The activated molecule has a certain average life period of excitation and if within this period it can collide with an acceptor molecule, chemical transformation may occur. The probability of collision within the life period of excitation (τ) will in the cases of solution increase as the osmotic pressure of the acceptor molecules in solution increases, until for a large concentration of the latter, all the activated molecules bring about chemical transformation by collision. The rate of chemical transformation for a constant rate of production of active molecules is given by

$$\frac{dx}{dt} = c\,\frac{\tau}{T+\tau} \qquad \text{...Eq. 2}$$

(Carvo, *Zeit. Physik*, 1922, **10**, 185 ; Turner, *Phys. Review*, 1924, **23**, 466).

Now the time period t between two successive collisions between an active uranyl nitrate molecule and leucobase molecule will, on the assumption that the kinetic theory of gases can be extended to dilute solutions, be given by the expression,

$$T = \frac{1}{Aa^s p}$$

where $A = 266\cdot 66\ \sqrt{\dfrac{2\pi N}{k\theta}\cdot\dfrac{m_1+m_2}{m_1-m_2}}$ a constant,

a the distance between the centres of two reacting molecules on collision and p the pressure of acceptor molecules expressed in millimetres of mercury. It is obvious that in order that T should remain constant during the progress of reaction, p should be kept constant. In our experiments total change was very small compared with the initial concentration of the base and its concentration therefore remained practically constant. The complete equation in our case is

$$\frac{dx}{dt} = kI_0\left[\,1-e^{-\epsilon c\,l}\,\right]\cdot\frac{1}{1+\dfrac{1}{Aa^s\tau p}} \qquad \text{...} \qquad \text{Eq. 3}$$

For weak absorption of light Eq. (8) transforms into

$$\frac{dx}{dt} = kI_0(a-x) \cdot \frac{1}{1 + \dfrac{1}{Aa^2\tau p}} \qquad \dots \qquad \text{Eq. 4}$$

If the change in a given reaction be very small compared with the initial concentration of the reacting substances Eq. (4) reduces itself to

$$\frac{dx}{dt} = kI_0 \cdot a \cdot \frac{1}{1 + \dfrac{1}{Aa^2\tau p}}$$

In our experiments the change in the concentration of uranyl nitrate during the course of the reaction was almost insignificant compared with the concentration of uranyl nitrate. Eq. (5) indicates that for a particular reaction where a and p are constant $\Delta x/\Delta t$ or the rate is also constant. The experimental results agree with this conclusion. Eq. (5) also shows that $\Delta x/\Delta t$ is directly proportional to each of the variable factors provided that p and one of the factors I_0 and a are constant. Our data agree with this conclusion. For constant rate of production of excited molecules, i.e., for constant light intensity and given uranyl nitrate concentration, the equation is

$$\frac{dx}{dt} \text{ or rate} = k \cdot \frac{}{1 + \dfrac{}{Aa^2\tau p}}$$

$$\text{or } \frac{1}{\text{Rate}} = \frac{1}{k} + \frac{1}{Aa^2\tau p} \cdot \frac{1}{k}$$

Therefore 1/Rate plotted against $1/p$ should be a straight line. The intercept of the graph is obviously

$$\frac{1}{k} \text{ and the slope } \frac{1}{k} \cdot \frac{1}{Aa^2\tau}$$

$$\text{Therefore } \frac{\text{Intercept}}{\text{Slope}} = Aa^2\tau.$$

$$\text{Intercept} = \cdot 6 \text{ and slope} = 6 \cdot 8 \times 10^3$$

$a = 2 \times 10^{11}$.   If $a = 3 \times 10^{-8}$ cm., τ becomes $4 \cdot 9 \times 10^{-11}$ sec.

Intercept $= 1 \cdot 2$ and slope $= 14 \times 10^{3}$ so that τ has the same value.

Temperature Coefficient of the Reaction.

It has been found that for an increase of 10°C from 22° to 32° the reaction rate remained practically the same. Hence so far as the temperature coefficient is concerned this reaction falls under the category of photochemical reactions having no temperature co-efficient.

Application of Einstein's Law of Photochemical Equivalence.

As this reaction has no temperature coefficient, its reaction rate varying directly as the intensity of light and uranyl nitrate concentration it was thought that Einstein's Law might be obeyed in this case. But actual calculation shows that more than one quantum is necessary to transform one molecule of leucobase and so the efficiency is less than unity.

TABLE V.

Conc. of uranyl nitrate $= M/2$

Rate for M/10 conc. of leuco-base $\dfrac{50 \times 10^{-6}}{60 \times 60}$ gm. moles. per.

sec. per litre.

Incident light intensity $= 400$ ergs.

Percentage of absorbed by M/2 uranyl nitrate concentration 1 mm. thick for wave-length limits 470—410 $\mu\mu = 13 \cdot 5$. Hence quantity of light absorbed per sq. cm. of the reaction cell per sec.

$$= \frac{13 \cdot 5}{100} \times 400 \text{ ergs.}$$

No. of quanta of incident blue light of average wave-length

$$440 \,\mu\mu = \frac{18 \cdot 5}{100} \times 400 \times \frac{440 \times 10^{-7}}{6 \cdot 55 \times 10^{-27} \times 3 \times 10^{10}} = 11 \cdot 7 \times 10^{12}.$$

No. of moles. transformed per sec. per 1 c.c. (for the depth was 1 mm.)

$$\frac{50 \times 10^{-6}}{60 \times 60} \times \frac{6 \cdot 06 \times 10^{23}}{1000 \times 10} = 8 \cdot 4 \times 10^{11}.$$

Therefore $\dfrac{\text{No. of quanta}}{\text{No. of moles}} = 14$ approximately.

This calculation is based on the statement due to Plotnikow that the filters used in this investigation transmitted mainly blue light and only a very negligible quantity of light of other wave-lengths. A thorough investigation to test the validity of this statement is now in progress. It is also intended to study the influence of pure monochromatic radiation obtained with the aid of a mono-chromator on this photosensitive system.

Effect of Different Wave-lengths on the Rate of Reaction.

By means of light filters (Plotnikow, *loc. cit.*) the action of the following monochromatic radiation was separately studied,—red 780-639$\mu\mu$; yellow 640-574 $\mu\mu$; green 540-505 $\mu\mu$; light blue 494-458 $\mu\mu$; dark blue 478-410 $\mu\mu$. The region 478-410 $\mu\mu$ was the most efficient. All the experimental data above recorded have been taken with this spectral region. Light blue had also some effect but it was very small compared with that due to dark blue ; effect of red radiation was very small whilst those of yellow and green nil.

It was thought that the dye after it has been formed might absorb radiation and accelerate further change, hence we should have auto-catalysis in white light. No such phenomenon has been observed. We also made one experiment in which after some dye has been formed by the action of dark blue light we changed the filters and red light was made to be incident upon it but no further reaction took place in a sufficient length of time. Hence light absorbed by the dye has no effect in the rate of change of the reaction.

Summary.

1.   The oxidation of the leucobase of malachite green by means of uranyl nitrate is purely a photochemical phenomenon.

2.   Spectral region 478-410 $\mu\mu$ is the most efficient radiation in bringing about the photochemical change.

3.   The photochemical oxidation has got no temperature coefficient.

4.   The reaction rate varies directly as the light intensity and as the concentration of uranyl nitrate.

5.   The inverse of reaction rate plotted against the inverse of the concentration of leucobase is a straight line, as demanded by Cairo-Turner equation.

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Extinction Coefficients of Mixtures of Uranyl Nitrate and Organic Acids in the Ultraviolet, as Experimental Evidence in Favour of the Formation of Unstable Intermediate Compounds.

By Jnanendra Chandra Ghosh and Bhupendra Nath Mitter.

It is well known that almost all organic acids undergo photo-chemical decomposition in presence of uranyl salts. The general mechanism of this photo-chemical reaction is not yet definitely settled, and this investigation was undertaken with the object of elucidating this problem.

Victor Henri (*Compt. rend.*, 1914, **158**, 181) has already observed that the extinction coefficient of mixtures of oxalic acid and uranyl salts in aqueous solution for wave-lengths in the ultraviolet is greater than the sum of the extinction coefficients of these solutions for the same radiation taken separately. No systematic work, however, has been done in the subject, and no clear explanation of this phenomenon has been offered.

If we accept the theory that a change in colour is due to a change in the nature of the molecular species, then it is not difficult to obtain a simple and quantitative explanation of this exaltation in the value of the extinction coefficients. Let us assume for the sake of simplicity that one molecule of uranyl nitrate (U) may combine with one molecule of an organic acid (A) to give us one molecule of the intermediate complex (M). Then applying the law of mass action, if x be the concentration of the intermediate complex, and U_1 and A_1 the initial concentration of uranyl nitrate and of the organic acid respectively,

$$[U_1 - x_1] \ [A_1 - x_1] = K x_1 \qquad (1)$$

At the same temperature the value of K should remain constant. Let E_U^λ, E_A^λ and E_M^λ be the molecular extinction coefficients for wave-length λ of the uranyl salt, the organic acid, and the

intermediate complex respectively. Then the observed extinction coefficient for the mixture

$$E_1^\lambda = E_U^\lambda \left[U_1 - x_1 \right] l + E_A^\lambda \left[A_1 - x_1 \right] l + E_M^\lambda \left[x_1 \right] l \quad (2)$$

where l is length of the solution through which light passes. For other dilutions,

$$E_2^\lambda = E_U^\lambda \left[U_2 - x_2 \right] l + E_A^\lambda \left[A_2 - x_2 \right] + E_M^\lambda \left[x_2 \right] l \quad (3)$$

and

$$\left[U_2 - x_2 \right] \quad A_2 - x_2 \right] = K x_2 \quad (4)$$

The values E_1^λ and E_2^λ, E_U^λ, E_A^λ, $[U_1]$, $[U_2]$, $[A_1]$, $[A_2]$

and l are experimentally measured magnitudes.

There are thus four unknown quantities x_1, x_2, K, and E_M^λ, and four equations, and hence their values can be determined. ' For any other wave-length, λ', since the value of K always remains the same, x can be easily calculated from equation (1) and therefore from a single measurement of extinction coefficient of mixture and of the components separately, it is possible to calculate the value of $E_M^{\lambda'}$, as will be clear from the following equation.

$$E^{\lambda'} = E_U^{\lambda'} \left[U - x \right] + E_A^{\lambda'} \left[A - x \right] + E_M^{\lambda'} \left[x \right]$$

From the tables given in the paper it will be seen that the experimental data of extinction coefficients of mixtures in most cases can be quantitatively explained—

(1) on the basis of an equilibrium in solution between the uranyl salt and organic 'acid as reactants and an intermediate complex formed by the loose combination of one molecule of each of the reactants, and

(2) on the assumption of a definite value of molecular extinction coefficients for each wave-length for the intermediate complex so formed.

EXPERIMENTAL.

The uranyl nitrate and the acids were carefully purified in the laboratory, and the extinction coefficients were measured with the aid of rotating sector photometer of Adam Hilger in conjunction with their quartz spectrograph.

Though the photographic density of the two spectra in juxtaposition can be compared fairly accurately still the probability of error in the value of the extinction coefficients is certainly $\pm$ 7 % .

The length of the tube containing the solution was 2 cm. in all the cases.

TABLE I.

M/2000 *Uranyl nitrate* (U) *and Formic Acid* (A); K=10.

	$\text{Log}\frac{I_0}{I}$ FOR WAVE-LENGTH (λ)				Conc. of int. complex as calculated.
	2770	2600	2545	2507	
M/2000 U	·25	·55	·6	·7	......
M acid	...	·1	·2	·5	
M/2000 U + M acid mixture ...	·35	·90	1·05	...	$·455 \times 10^{-2}$
E calc.	·34	·92	1·07	...	
M/5 acid	...	...	·05	·1	
M/2000 U + M/5 acid mixture ...	·30	·75	·85	1·2	$·33 \times 10^{-2}$
E calc.	·32	·75	·85	1·8	
M/10 acid	..	...	...	·05	
M/2000 U + M/10 acid mixture	·30	·7	·75	1·05	$·25 \times 10^{-2}$
E calc.	·30	·7	·75	1·05	
M/20 acid	...	...	...	...	
M/2000 U + M/20 acid mixture	·25	·65	·7	·9	$·165 \times 10^{-2}$
E calc.	·28	·65	·7	·9	
M/50 acid	...	...	...	...	
M/2000 U + M/50 acid mixture	·25	·6	·65	·80	$·083 \times 50^{-2}$
E calc.	·27	·6	·65	·80	

In calculating the values of E for the various mixtures K has been assumed to be 10 in all the cases and E_M^λ given the following values for various wave-lengths—

λ =	2770	2600	2545	2507
E_M =	$\cdot 10 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 60 \times 10^3$

With M/1000 conc. of uranyl nitrate and varying conc. of formic acid, extinction coefficients could be measured for higher wave-lengths and the observed values of extinction coefficients for mixtures could be reproduced by assuming $K=10$ and

λ =	2961	2770	2600
E_M =	$\cdot 06 \times 10^3$	$\cdot 10 \times 10^3$	$\cdot 30 \times 10^3$

TABLE II.

M/2000 *Uranyl nitrate* (U) *and Acetic acid* (A); $K=6$.

	$\mathrm{Log.}\frac{I_0}{I_t}$ FOR WAVE-LENGTH (λ)				Conc. of int. complex (x) as calculated.
	2770	2722	2600	2545	
M/2000 U ...	$\cdot 25$	$\cdot 3$	$\cdot 55$	$\cdot 6$	
[4M acid ...	$\cdot 1$	$\cdot 2$	$\cdot 3$	$\cdot 4$	
Mixture ...	$\cdot 75$	$1 \cdot 0$	$1 \cdot 45$	...	$\cdot 48 \times 10^{-2}$
E calc. ...	$\cdot 74$	$1 \cdot 01$	$1 \cdot 45$	...	
M acid ...	...	...	$\cdot 1$	$\cdot 1$	
Mixture ...	$\cdot 6$	$\cdot 75$	$1 \cdot 2$	$1 \cdot 40$	$\cdot 429 \times 10^{-2}$
E calc. ...	$\cdot 6$	$\cdot 75$	$1 \cdot 19$	$1 \cdot 39$	
M/2 acid ...	...	...	...	$\cdot 05$	
Mixture ...	$\cdot 55$	$\cdot 7$	$1 \cdot 0$	$1 \cdot 25$	$\cdot 375 \times 10^{-2}$
E calc. ...	$\cdot 56$	$\cdot 7$	$1 \cdot 02$	$1 \cdot 25$	
M/10 acid ...	...	...	...	...	
Mixture ...	$\cdot 4$	$\cdot 5$	$\cdot 80$	$\cdot 9$	$\cdot 188 \times 10^{-2}$
E calc. ...	$\cdot 4$	$\cdot 5$	$\cdot 79$	$\cdot 9$	
M/50 acid ...	...	...	...	...	
Mixture ...	$\cdot 3$	$\cdot 35$	$\cdot 60$	$\cdot 70$	$\cdot 053 \times 10^{-2}$
E calc. ...	$\cdot 29$	$\cdot 35$	$\cdot 62$	$\cdot 68$	

In calculating the values of E^λ for the various mixtures K has been assumed to be 6 in all the cases and E_M^λ given the following values for various wave-lengths—

λ =	2770	2722	2600	2545
E_M =	$\cdot41 \times 10^3$	$\cdot58 \times 10^3$	$\cdot68 \times 10^3$	$\cdot80 \times 10^3$

With M/1000 conc. of uranyl nitrate and varying conc. of acetic acid, extinction coefficients could be measured for higher wave-lengths and the observed values of extinction coeff. could be reproduced by assuming $K=6$ and

λ =	2961	2770	2722	2600
E_M =	20×10^3	$\cdot40 \times 10^3$	$\cdot54 \times 10^3$	$\cdot64 \times 10^3$

TABLE III.

M/2000 *Uranyl nitrate* (U) *and Propionic Acid* (A); $K=4$.

	$\text{Log} \frac{I_o}{I_t}$ FOR WAVE-LENGTH (λ)				x calculated.
	2770	2600	2545	2507	
M/2000 U ...	$\cdot25$	$\cdot55$	$\cdot6$	$\cdot7$	
M/5 acid ...	...	...	$\cdot1$	$\cdot15$	
Mixture ...	$\cdot55$	$1\cdot10$	$1\cdot25$	...	$\cdot22 \times 10^{-3}$
E calc. ...	$\cdot54$	$1\cdot11$	$1\cdot26$	...	
M/10 acid ...	...	...	$\cdot05$	$\cdot1$	
Mixture ...	$\cdot45$	$\cdot90$	$1\cdot00$	$1\cdot2$	$\cdot143 \times 10^{-3}$
E calc. ...	$\cdot44$	$\cdot91$	$1\cdot01$	$1\cdot2$	
M/20 acid ...	...	...	...	...	
Mixture ...	$\cdot35$	$\cdot75$	$\cdot80$	$\cdot95$	$\cdot083 \times 10^{-3}$
E calc. ...	$\cdot35$	$\cdot76$	$\cdot81$	$\cdot93$	
M/50 acid ...	...	...	...	...	
Mixture ...	$\cdot3$	$\cdot65$	$\cdot70$	$\cdot8$	$\cdot038 \times 10^{-3}$
E calc. ...	$\cdot3$	$\cdot64$	$\cdot69$	$\cdot8$	
M/100 acid ...	...	...	...	...	
Mixture ...	$\cdot25$	$\cdot6$	$\cdot65$	$\cdot75$	$\cdot019 \times 10^{-3}$
E calc. ...	$\cdot27$	$\cdot6$	$\cdot65$	$\cdot75$	

In calculating the values of E, K has been assumed to be 4 and the following values of E_M^λ given—

λ	=	2770	2600	2545	2507
E_M	=	$\cdot 66 \times 10^3$	$1\cdot 26 \times 10^3$	$1\cdot 26 \times 10^3$	$1\cdot 39 \times 10^3$

With M/1000 conc. of uranyl nitrate and different conc. of propionic acid, extinction coefficients could be measured for higher wave-lengths and the observed values of E could be reproduced by assuming $K=4$ and

λ	=	2961	2770	2600
E_M	=	$\cdot 34 \times 10^3$	$\cdot 66 \times 10^3$	$1\cdot 23 \times 10^3$

TABLE IV.
M/2000 *Uranyl nitrate* (U) *and Oxalic acid* (A); $K=115$.

		$\text{Log}\frac{I_0}{I_t}$. FOR WAVE-LENGTH ($\lambda$) :			x calculated.
		3364	3274	2961	
M/2000 U	...	...	...	$\cdot 15$	
M/10 acid	...	...	$\cdot 1$	$\cdot 6$	
Mixture	...	$\cdot 25$	$\cdot 6$	...	$\cdot 460 \times 10^{-3}$
E calc.	...	$\cdot 24$	$\cdot 6$	...	
M/20 acid	...	...	$\cdot 05$	$0\cdot 3$	
Mixture	...	$\cdot 25$	$\cdot 55$	$1\cdot 40$	$\cdot 426 \times 10^{-3}$
E calc.	...	$\cdot 22$	$\cdot 52$	$1\cdot 37$	
M/40 acid	...	...	...	$\cdot 15$	
Mixture	..	$\cdot 20$	$\cdot 4$	$1\cdot 1$	$\cdot 371 \times 10^{-3}$
E calc.	...	$\cdot 19$	$\cdot 4$	$1\cdot 1$	
M/100 acid	...	...	...	...	
Mixture	...	$\cdot 15$	$\cdot 3$	$\cdot 75$	$\cdot 266 \times 10^{-3}$
E calc.	...	$\cdot 14$	$\cdot 3$	$\cdot 73$	
M/200 acid	...	...	...	...	
Mixture	...	$\cdot 1$	$\cdot 2$	$\cdot 55$	$\cdot 182 \times 10^{-3}$
E calc.	...	$\cdot 1$	$\cdot 2$	$\cdot 55$	

In calculating the values of E, K has been assumed to be 115 in all the cases and the following values E_M^λ given—

$$\lambda \quad = \quad 3364 \quad\quad 3274 \quad\quad 2961$$
$$E_M \quad = \quad \cdot 27 \times 10^3 \quad \cdot 55 \times 10^3 \quad 1\cdot 08 \times 10^3$$

With M/1000 conc. of U and different conc. of oxalic acid E could be measured for higher wave-lengths with $K = 115$ and

$$\lambda \quad = \quad 3435 \quad\quad 3364 \quad\quad 3274 \quad\quad 2961$$
$$E_M \quad = \quad \cdot 145 \times 10^3 \quad \cdot 27 \times 10^3 \quad \cdot 55 \times 10^3 \quad 1\cdot 08 \times 10^3$$

TABLE V.

M/2000 *Uranyl nitrate* (U) *and Malonic acid* (A); $K = 80$.

	$\mathrm{Log}\frac{I_o}{I_t}$ FOR WAVE-LENGTH (λ).				x calculated.
	2961	2770	2722	2600	
M/2000 U ...	·15	·25	·3	·55	
M/10 acid ...	...	...	...	...	
Mixture ...	·35	·85	1·1	...	·44 × 10⁻³
E calc. ...	·36	·86	1·1	...	
M/20 acid ...	...	...	...	...	
Mixture ...	·35	·8	1·0	...	·4 × 10⁻³
E calc. ...	·34	·8	1·0	...	
M/40 acid ...	...	...	...	...	
Mixture ...	·30	·70	·9	...	·33 × 10⁻³
E calc. ...	·31	·71	·9	...	
M/100 acid ...	...	...	...	...	
Mixture ...	·25	·55	·7	1·25	·22 × 10⁻³
E calc. ...	·26	·56	·7	1·25	
M/200 acid ...	...	...	...	...	·143 × 10⁻³
Mixture ...	·20	·45	·55	1·0	
E calc. ...	·21	·45	·55	1·0	

In calculating the values of E, K has been assumed to be 80 in all the cases, and the following values of E_M^λ for various wave-lengths given—

λ =	2961	2770	2722	2600
E_M =	$\cdot24 \times 10^3$	$\cdot69 \times 10^3$	$\cdot90 \times 10^3$	$1\cdot60 \times 10^3$

With M/1000 conc. of U and different conc. of malonic acid the following value of E_M^λ reproduced extinction coefficients for various mixtures with $K = 80$.

λ =	3274	2961	2770
E_M =	$\cdot12 \times 10^3$	$\cdot22 \times 10^3$	$\cdot69 \times 10^3$

TABLE VI.

M/2000 *Uranyl nitrate* (U) *and Succinic acid* (A) ; $K = 50$.

	$\text{Log}\frac{I_o}{I_t}$ FOR WAVE-LENGTH (λ)				x calculated.
	2770	2600	2545	2507	
M/2000 U ...	$\cdot25$	$\cdot55$	$\cdot6$	$\cdot7$	
M/10 acid ...	...	...	$\cdot05$	$\cdot1$	
Mixture ...	$\cdot50$	$1\cdot00$	$1\cdot1$	$1\cdot4$	$\cdot416 \times 10^{-3}$
E calc. ...	$\cdot47$	$\cdot97$	$1\cdot07$	$1\cdot4$	
M/20 acid ...	...	...	...	$\cdot05$	
Mixture ...	$\cdot46$	$\cdot90$	$\cdot95$	$1\cdot25$	$\cdot357 \times 10^{-3}$
E calc. ...	$\cdot44$	$\cdot91$	$\cdot96$	$1\cdot23$	
M/40 acid ...	...		...	...	
Mixture ...	$\cdot40$	$\cdot85$	$\cdot90$	$1\cdot1$	$\cdot277 \times 10^{-3}$
E calc. ...	$\cdot39$	$\cdot83$	$\cdot88$	$1\cdot1$	
M/100 acid ...	...	...	...	...	
Mixture ...	$\cdot35$	$\cdot70$	$\cdot75$	$\cdot95$	$\cdot166 \times 10^{-3}$
E calc. ...	$\cdot34$	$\cdot72$	$\cdot77$	$\cdot94$	
M/200 acid ...	...	...	...	...	
Mixture ...	$\cdot3$	$\cdot65$	$\cdot7$	$\cdot85$	$\cdot100 \times 10^{-3}$
E calc. ...	$\cdot3$	$\cdot65$	$\cdot7$	$\cdot84$	

•In calculating the values of E, K has been assumed to be 50 and the following values of E_M^λ given—

$\lambda =$	2770	2600	2545	2507
$E_M =$	$\cdot 28 \times 10^3$	$\cdot 53 \times 10^3$	$\cdot 53 \times 10^3$	$\cdot 75 \times 10^3$

With M/1000 conc. of U and different concentrations of succinic acid E could be measured for higher wave lengths with $K=50$ and

$\lambda =$	3274	2961	2770	2600
$E_M =$	$\cdot 18 \times 10^3$	$\cdot 21 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 53 \times 10^3$

TABLE VII.

M/2000 *Uranyl nitrate* (U) *and Glycollic acid* (A); $K=15$.

	$\text{Log} \frac{I_o}{I_t}$ FOR WAVE-LENGTH (λ).				x calculated.
	2770	2722	2600	2545	
M/2000 U ...	·25	·3	·55	·6	
M/5 acid ...	·3	·3	·3	·35	
Mixture ...	·85	1·1	1·45	...	·375 × 10⁻³
E calc. ...	·85	1·1	1·46	...	
M/20 acid ...	·05	·05	·05	·1	
Mixture ...	·45	·65	·95	1·2	·214 × 10⁻³
E calc. ...	·44	·64	·95	1·2	
M/50 acid ...	...	...	...	...	
Mixture ...	·35	·45	·75	·90	·115 × 10⁻³
E calc. ...	·34	·45	·74	·86	
M/100 acid ...	...	...	...	...	
Mixture ...	·3	·40	·65	·75	·065 × 10⁻³
E calc. ...	·3	·39	·65	·75	
M/200 acid ...	...	...	...	...	
Mixture ...	·25	·35	·60	·70	·035 × 10⁻³
E calc. ...	·28	·35	·61	·68	

In calculating the values of E, K has been assumed to be 15 and the following values of E_M^λ given—

$\lambda =$	2770	2722	2600	2545
E_M	$\cdot41 \times 10^3$	$\cdot67 \times 10^3$	$\cdot82 \times 10^3$	$1\cdot15 \times 10^3$

With M/1000 conc. of U and various conc. of glycollic acid E could be measured for higher wave-lengths with $K = 15$ and

$\lambda =$	3274	2961	2770	2722	2600
$E_M =$	$\cdot13 \times 10^3$	$\cdot17 \times 10^3$	$\cdot40 \times 10^3$	$\cdot63 \times 10^3$	$\cdot82 \times 10^3$,

TABLE VIII.

M/2000 *Uranyl nitrate* (U) *and Lactic acid* (A); $K = 10$.

		Log $\frac{I_o}{I_t}$ for wave-length (λ).				x calculated.
		2961	2770	2600	2545	
M/2000 U	...	$\cdot15$	$\cdot25$	$\cdot55$	$\cdot6$	
M acid	...	...	$\cdot2$	$\cdot4$	$\cdot5$	
Mixture	...	$\cdot40$	$1\cdot0$	...	...	$\cdot455 \times 10^{-3}$
E calc.	...	$\cdot42$	$1\cdot0$	...	...	
M/5 acid	...	...	...	$\cdot05$	$\cdot1$	
Mixture	...	$\cdot35$	$\cdot65$	$1\cdot25$	$1\cdot5$	$\cdot330 \times 10^{-3}$
E calc.	...	$\cdot35$	$\cdot65$	$1\cdot26$	$1\cdot5$	
M/10 acid	...	...	...	...	$\cdot05$	
Mixture	...	$\cdot3$	$\cdot55$	$1\cdot05$	$1\cdot25$	$\cdot250 \times 10^{-3}$
E calc.	...	$\cdot3$	$\cdot55$	$1\cdot05$	$1\cdot25$	
M/20 acid	...	...	...	...	...	
Mixture	...	$\cdot25$	$\cdot45$	$\cdot90$	$1\cdot0$	$\cdot165 \times 10^{-3}$
E calc.	...	$\cdot25$	$\cdot45$	$\cdot88$	$1\cdot0$	
M/50 acid	...	...	...	...	...	
Mixture	...	$\cdot2$	$\cdot35$	$\cdot70$	$\cdot8$	$\cdot063 \times 10^{-3}$
E calc.	...	$\cdot2$	$\cdot35$	$\cdot71$	$\cdot8$	

In calculating the values of E, K has been assumed to be 10 and the following values of E_M^λ given—

$\lambda =$	2961	2770	2600	2545
E_M	$\cdot 30 \times 10^3$	$\cdot 60 \times 10^3$	$1 \cdot 00 \times 10^3$	$1 \cdot 20 \times 10^3$.

With M/1000 conc. of U and different conc. of lactic acid E could be measured for higher wave-lengths with $K = 10$ and

$\lambda =$	3274	2961	2770
$E_M =$	$\cdot 21 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 60 \times 10^3$

TABLE IX.

M/2000 *Uranyl nitrate* (U) *and Tartaric acid* (A); $K = 20$.

	$\text{Log} \frac{I_o}{I_t}$ FOR WAVE-LENGTH (λ).				x calculated.
	2961	2770	2600	2545	
M/2000 U ...	$\cdot 15$	$\cdot 25$	$\cdot 55$	$\cdot 6$	
M/10 acid ...	...	...	$\cdot 1$	$\cdot 1$	
Mixture ...	$\cdot 45$	$\cdot 65$	$1 \cdot 45$	...	$\cdot 33 \times 10^{-3}$
E calc. ...	$\cdot 45$	$\cdot 64$	$1 \cdot 44$	...	
M/20 acid ...	...	...	$\cdot 05$	$\cdot 05$	
Mixture ...	$\cdot 35$	$\cdot 55$	$1 \cdot 20$	$1 \cdot 45$	$\cdot 25 \times 10^{-3}$
E calc ...	$\cdot 37$	$\cdot 54$	$1 \cdot 19$	$1 \cdot 45$	
M/40 acid ...	...	...	...	...	
Mixture ...	$\cdot 3$	$\cdot 45$	$\cdot 95$	$1 \cdot 15$	$\cdot 165 \times 10^{-3}$
E calc ...	$\cdot 3$	$\cdot 44$	$\cdot 94$	$1 \cdot 13$	
M/100 acid ...	...	...	...	...	
Mixture ...	$\cdot 20$	$\cdot 35$	$\cdot 75$	$\cdot 85$	$\cdot 083 \times 10^{-3}$
E calc. ...	$\cdot 22$	$\cdot 35$	$\cdot 75$	87	
M/200 acid ...	...	...	...	...	
Mixture ...	$\cdot 20$	$\cdot 3$	$\cdot 65$	$\cdot 75$	$\cdot 045 \times 10^{-3}$
E calc. ...	$\cdot 19$	$\cdot 3$	$\cdot 65$	$\cdot 75$	

In calculating the values of E, K has been assumed to be 20 and the following values of E_M^λ given—

λ	=	2961	2770	2600	2545
E_M	=	$\cdot44 \times 10^3$	$\cdot58 \times 10^3$	$1\cdot18 \times 10^3$	$1\cdot60 \times 10^3$

With M/1000 conc. of U and different conc. of tartaric acid E could be measured for higher wave-lengths with $K=20$ and

λ	=	3364	3274	2961	2770
E_M	=	$\cdot30 \times 10^3$	$\cdot45 \times 10^3$	$\cdot45 \times 10^3$	$\cdot60 \times 10^3$

TABLE X.

M/2000 *Uranyl nitrate* (U) *and Mandelic acid* (A); $K=50$.

		$\text{Log}\ \frac{I_0}{I_t}$, FOR WAVE-LENGTH ($\lambda$).				Conc. of int. complex as calculated.
		3274	2961	2770	2722	
M/2000 U	...	...	$\cdot15$	$\cdot25$	$\cdot3$	......
M/10 acid	...	...	...	$\cdot4$	...	
Mixture	...	$\cdot25$	$\cdot55$	$1\cdot25$	...	$\cdot415 \times 10^{-3}$
E calc.	...	$\cdot25$	$\cdot55$	$1\cdot25$	...	
M/20 acid	...	...	...	$\cdot2$	$1\cdot5$	
Mixture	...	$\cdot20$	$\cdot50$	$\cdot95$	...	$\cdot357 \times 10^{-3}$
E calc.	...	$\cdot21$	$\cdot49$	$\cdot96$	...	
M/50 acid	...	...	...	$\cdot05$	$\cdot6$	
Mixture	...	$\cdot15$	$\cdot40$	$\cdot65$	...	$\cdot25 \times 10^{-3}$
E calc.	...	$\cdot15$	$\cdot39$	$\cdot66$	...	
M/100 acid	...	...	...	...	$\cdot3$	
Mixture	...	$\cdot1$	$\cdot3$	$\cdot5$	$1\cdot00$	$\cdot165 \times 10^{-3}$
E calc.	...	$\cdot1$	$\cdot3$	$\cdot5$	$\cdot98$	
M/200 acid	...	...	...	...	$\cdot15$	
Mixture	...	...	$\cdot25$	$\cdot40$	$\cdot65$	$\cdot10 \times 10^{-3}$
E calc.	...	...	$\cdot24$	$\cdot39$	$\cdot68$	

In calculating the values of E for the various mixtures, K has been assumed to be 50 in all the cases, and E_M^λ given the following values for various wave-lengths—

λ	=	3274	2961	2770	2722
E_M	=	$\cdot 30 \times 10^3$	$\cdot 48 \times 10^3$	$\cdot 72 \times 10^3$	$1 \cdot 15 \times 10^3$

With M/1000 conc. of uranyl nitrate and varying conc. of mandelic acid, extinction coeff. could be measured for higher wave-lengths and the observed values of extinction coeffs. for mixtures could be reproduced by assuming $K = 50$ and

λ	=	3435	3364	3274	2961	2770
E_M	=	$\cdot 15 \times 10^3$	$\cdot 24 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 48 \times 10^3$	$\cdot 71 \times 10^3$

Certain regularities have been found between the values of dissociation constant (K) of intermediate complex formed by the combination of uranyl nitrate and organic acid and the constitution of that acid :

1. In a homologous series the value of K diminishes as we go higher up the series in a definite ratio for each addition of a (CH_2) group—

$$\frac{\text{Formic}}{\text{Acetic}} = \frac{10}{6} = 1 \cdot 66 ; \qquad \frac{\text{Acetic}}{\text{Propionic}} = \frac{6}{4} = 1 \cdot 5 ;$$

$$\frac{\text{Oxalic}}{\text{Malonic}} = \frac{115}{80} = 1 \cdot 45 ; \qquad \frac{\text{Malonic}}{\text{Succinic}} = \frac{80}{50} = 1 \cdot 6.$$

2. The value of K increases about 12 times as the hydrogen atom of a (CH_2) group is replaced by a $(COOH)$ group—

$$\frac{\text{Oxalic}}{\text{Formic}} = \frac{115}{10} = 11 \cdot 5 ; \qquad \frac{\text{Malonic}}{\text{Acetic}} = \frac{80}{6} = 13 \cdot 3 ; \qquad \frac{\text{Succinic}}{\text{Propionic}} = \frac{50}{4} = 12 \cdot 5.$$

3. In the case of monobasic acids, replacement of a hydrogen atom in a (CH_2) group by (OH) group increases the value of dissociation constant $2 \cdot 5$ times.

$$\frac{\text{Glycollic}}{\text{Acetic}} = \frac{15}{6} = 2 \cdot 5 ; \qquad \frac{\text{Lactic}}{\text{Propionic}} = \frac{10}{4} = 2 \cdot 5.$$

Investigations on the behaviour of aromatic acids in presence of uranyl nitrate could not be carried out as these aromatic acids are sparingly soluble in water and their extinction coefficients in near ultraviolet have very large values.

Investigations are in progress with a view to find out by this method if the photochemical oxidation of organic acids by ferric salts is preceded by the formation of an intermediate compound.

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Gas Volumetric Estimation of SOOH in Organic Sulphinic Acids.

By S. Krishna and Bhagwan Das.

The characteristic property of the carboxyl group in organic acids is that it liberates iodine from a mixture of pure potassium iodide and iodate, and the reaction proceeds more or less quantitatively accordingly to the equation.—

$$6R.COOH + 5KI + KIO_3 = 6R.COOK + 3I_2 + 3H_2O.$$
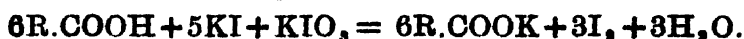
The iodine can be quickly and accurately determined by measuring the volume of oxygen which it liberates on treating it with a freshly prepared alkaline solution of hydrogen peroxide :

$$I_2 + 2KOH + H_2O_2 = 2KI + 2H_2O + O_2.$$
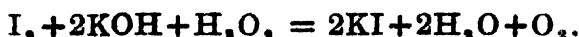
As in most cases the liberation of iodine by the action of organic acids on alkali iodide and iodate is slower than the mineral acids, so Kux (*Zeit. anal. Chem.*, 1893, **32**, 129) investigated the different conditions under which the common organic acids (R.COOH) could be estimated quantitatively by gas volumetric iodine process. The reaction usually proceeds at ordinary temperatures, but in certain cases the reaction is rather slow, but is appreciably accelerated by the action of heat.

The method has also been employed successfully in case of certain derivatives of the acids that contain positive groups. But it fails when such negative groups as sulphonic, sulphinic, nitro or hydroxyl are present. The reason obviously being that these also liberate iodine from the mixture of potassium iodide and iodate, and in certain cases, it has been noticed that the liberated iodine reacts very quickly with the compound replacing the original group altogether. Experiments in this direction have been carried out by Datta and Bhoumic (*J.Amer. Chem. Soc.*, 1921, **43**, 303) who have found that when a current of chlorine gas is introduced into an aqueous solution of sulphinic acid, the sulphinic group

is detached with the simultaneous production of the corresponding chloro-derivatives.

$$SO_2 < \begin{matrix} OH \\ X \end{matrix} + \begin{matrix} Cl \\ Cl \end{matrix} + \begin{matrix} H \\ OH \end{matrix} = SO_2 < \begin{matrix} OH \\ OH \end{matrix} + XCl + HCl$$
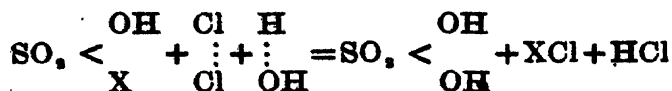
where X represents the organic radicle to which the sulphonic group is attached.

It has also been found that aromatic bodies which already contain an hydroxy group, as in the case of phenols and oxy-acids, exhibit a special facility in the displacement of sulphonic group by chlorine : thus anisole and phenetole sulponic acids have given tetrachloro-ketodihydrobenzene.
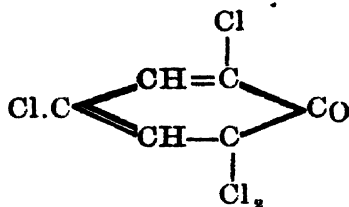
Pope and Wood (*J. Chem. Soc.*, 1912, **101**, 1827) found that a mixture of alkali bromide and bromate acts better' in the replacement of sulphonic groups, though in some cases it cause; an oxidising effect especially if there are easily oxidisable groups, *para* or *ortho* to each other ; for example, aniline sulphonic acid gives chloro-quinone.

From the above discussion it was concluded that the action of potassium iodide and iodate on aromatic sulphonic acids was not always in accordance with the Kux's equation, but instead it effected the replacement of sulphonic group and at the same time' produced a compound containing iodine in the benzene nucleus. Similar results have been obtained by Krishna and Pope on the action of KI and KI₃ on some hydroxy acids (*J. Chem. Soc.*, 1922, **121**, 798). From their experiments on salicylic acid, *p*-hydroxy benzoic acid, 3:5-nitro-salicylic acid and 3:5-dinitro-salicylic acid, it was found that the amount of iodine liberated fell much below the quantity demanded by Kux's iodine equation. It has been found that in each case the COOH group is completely removed from the nucleus and its place is taken up by iodine that is produced during the reaction, the corresponding tri-iodophe-

nol being produced in each case. This brings the reaction into agreement with the well known case of the replacement of acidic groups in aromatic sulphonic acids. Therefore under these circumstances, it is not possible to determine the carboxyl group by the usual Kux's method.

The present work has been conducted to study similar reactions with organic sulphinic acids. It has been found that when an aqueous solution of potassium iodide and iodate in certain proportions is added to an aqueous solution of benzene sulphinic acid, there is an evolution of free iodine, shown by the colour produced, which has been found to be in agreement with the equation,

$$6RSO_2H + 5KI + KIO_3 = 6RSO_2K + 3I_2 + 3H_2O.$$

The reaction has been investigated in the case of the following sulphinic acids, which were prepared according to the well-known methods.

Acids.	M. p.	References.
Benzene sulphinic acid	85°	Gattermann, *Ber.*, 1899, **32**, 1141.
p-Tolyl sulphinic acid.	86 87°	Do.
p-Dichlorobenzene sulphinic acid.	180-82°	Stewart, *J. Chem. Soc.*, 1922, **121**, 2557.
p-Chlornitrobenzene-o-sulphinic acid.	139°	Krishna, *J. Chem. Soc.*, 1923, **123**, 157.
m-Sulphinobenzoic acid.	197-98°	Gattermann, *loc. cit.*
p-Dibromobenzene sulphinic acid.	140°	Do.
p-Chlorbenzene sulphinic acid.	93-94°	Do.
p-Methoxy tolylsulphinic acid.	97-98°	Do. p. 1143.
p-Sulphino-acetanilide.	160°	Stewart, *loc. cit.*
5-Sulphino-salicylic acid.	159°	Do.
m-Benzene disulphinic acid.	118-19°	Autenreith, *Ber.*, 1903, **36**, 189.
p-Sulphino-cinnamic acid.	140-42°	Stewart, *loc. cit.*, p. 2560.
p-Bromobenzene sulphinic acid.	117°	Do.
p-Anisol sulphinic acid.	98°	Smiles, *J. Chem. Soc.*, 1922, **121**, 2858.

Acids.	M. p.	References.
p-Phenetol sulphinic acid ...	104—106°	Gattermann, *loc. cit.* p. 1144.
p-Nitro-toluene sulphinic acid ...	...	......
Naphthalene sulphinic acid ...	104—105°	Gattermann, *loc. cit.*
p-Sulphino phenyl acetic acid ...	142°	Smiles, *loc. cit.*
Guaiacol sulphinic acid.	...	......

In all the cases studied there is no detachment of the sulphinic group from the molecule, as has been observed in the case of sulphonic group, nor is there any evidence of the production of iodo derivatives. Therefore Kux's gas volumetric method can be applied for the quantitative estimation of sulphinic group. The reaction proceeds normally at the room temperature (15—20°C), undue rise of temperature having a deterimental effect due to the loss of iodine.

The general factors essential to the success of the experiment are the purity of the reagents, and an approximate adjustment of the proportions in which these are mixed. Potassium iodide and iodate used must be acid free. It is found advisable not to use more than double the theoretical quantity of hydrogen peroxide and about six times the theoretical amount of potash. A freshly made solution of one part of potassium hydroxide free from carbonates, in one part of distilled water (free from carbon dioxide) and 2 to 3 % solution of hydrogen peroxide were found to yield the best results.

The method of procedure in the beginning was conducted on the lines of Kux's iodine method. It was found that on adding a warm (50—80°) solution of the acids in small portions at a time to a warm aqueous solution of potassium iodide and iodate (in proportions demanded by the equation given above) and digesting the mixture on the water-bath for some time (usually twenty minutes) the amount of iodine liberated fell much below the quantity demanded by the equation and involved an error of more than 25% in many cases. Heating or longer digestion were therefore found to be inadmissible, and instead an ice cold aqueous acid solution added to an ice cold mixture of potassium iodide and

iodate, and this brought to the room temperature (18-20°) was found to yield the best results.

An attempt has been made to explain the mechanism of the reaction. Very probably, the first step in the reaction is the formation of a sulphonyl iodide :

$$R. SOOH + I_2 = R. SOOI + HI$$

which reacts further with the alkaline hydrogen peroxide and liberates the requisite amount of oxygen.

$$R. SOOI + H_2O_2 + 2KOH = R. SOOK + KI + 2H_2O + O_2$$

That sulphonic iodide is the first product of reaction is shown by the fact that on addition of potassium iodide and potassium iodate solution to sulphinic acid a thick yellow precipitate always results as has been isolated in many cases and found to be sulphonic iodides. Instances of the formation of sulphonic iodides have been found by Hinsberg (*Ber.*, 1908, **41**, 2836). The iodides have been found to be rather unstable bodies which break up into free iodine and the acid, thereby attaining an equilibrium. The free iodine liberated can be estimated by the usual method with standard thiosulphate solution, but only in such cases where the liberation of iodine is complete and there is no formation of intermediate sulphonic iodides, but where the iodide has not completely decomposed into iodine and acid, and the liberation of iodine is not quantitative, it is not possible to estimate the free iodine with thiosulphate solution.

In some cases in the solutions a white precipitate is observed and this probably is a disulphone. Instances of the formation of these disulphones have been found by Hinsberg (*loc. cit.*) where he has investigated that organic sulphides are converted into sulphoxides and disulphoxides (R. SO_2S. R) which absorb oxygen and get converted into disulphones. A reference may also be made to the work of Hilditch (*J. Chem. Soc.*, 1908, II, 1524) in this connection. In the present case the formation of disulphones may be represented according to the equation :

$$R. SO_2H + I_2 = R. SO_2I + HI$$
$$R. SO_2I + R. SO_2Na = RSO_2. SO_2R + NaI$$
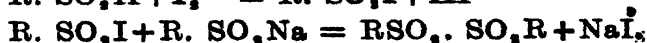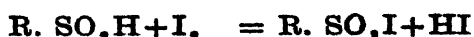
Another evidence of the formation of disulphones may be gathered from the following facts. In all the cases studied, it was noticed

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that the volume of oxygen in the Lunge nitrometer had to be recorded just a couple of minutes after the completion of the reaction as further delay involved an absorption of about 2 c. c. of oxygen in an hour's duration. This fact may therefore be explained on the conversion of sulphinic acid to sulphoxides and disulphones.

$$R. SO_2H + OH. SO. R = R. SO_2 - SO. R + H_2O$$
$$R. SO_2 - SO.R + O = R SO_2. SO_2R.$$
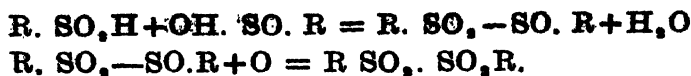
From the above discussion it is clear that Kux's gas volumetric method for the estimation of carboxyl group in organic acids, can, with slight experimental modifications, be successfully applied in the determination of -SOOH group in sulphinic acids, which have in the nucleus such groups as -NO$_2$, -Cl, -Br, -OH, -CH$_3$, -OCH$_3$, -COOH, -CH:CH.COOH, CH$_2$. COOH, -NH.CO.CH$_3$, -OC$_2$H$_5$.

In all such cases where another sulphinic group or a carboxyl group is present in the molecule, the oxygen liberated is double the usual volume, since both the groups now take part in the reaction.

EXPERIMENTAL.

Sulphinic acids were prepared by the usual methods from the corresponding sulphonyl chlorides. As the literature on the subject does not give complete details for obtaining sulphinic acids in good yields, it is thought desirable to give an account of a typical redution of the sulphonyl chlorides to the corresponding sulphinic acids.

A mixture of 20 gms. of the sulphonyl chloride and 50 gms. of sodium sulphite (Na$_2$SO$_3$, 9H$_2$O) and 100 gms. of crushed ice was shaken for three hours, until the sulphonyl chloride had dissolved. The mixture was tested for alkalinity from time to time and dilute sodium hydroxide was added to prevent formation of sulphur dioxide. The mixture was kept cold by further addition of ice, any undue increase of temperature being fatal to the success of the experiment on account of hydrolysis of the sulphonyl chloride. The mixture was filtered, and acidified slowly with cold concentrated hydrochloric acid, when sulphinic acids (usually crystalline) separated. The yield of sulphinic acid is in almost all cases about 80-90 per cent. Recrystallised acids were thoroughly dried by keeping them in vacuum desiccator before using. These gave the usual test with phenetole and sulphinic acid (Smiles' test).

About 0·2 gm. of well powdered sulphinic acid which had been thoroughly dried by keeping in a vacuum desiccator for two days was dissolved in 40 c.c. of hot water and cooled in ice. To this was added in small portions at a time an ice cold mixture of potassium iodide (2 g.) and potassium iodate (0·2 g.). The mixture was brought to the room temperature and washed into an outer vessel A of the apparatus
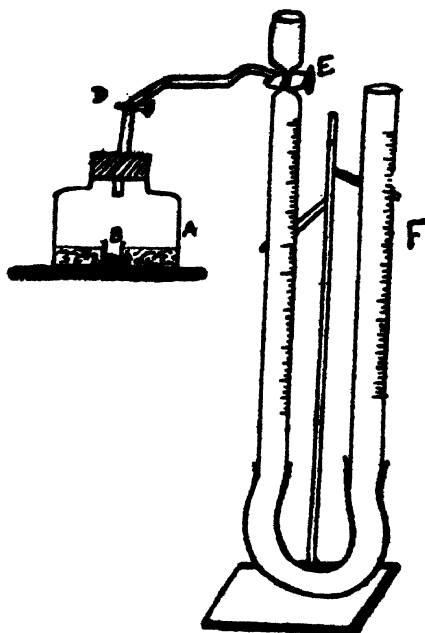
shown. Into the inner vessel B was put a freshly made and cooled mixture of 2 c.c. of 3 per cent. hydrogen peroxide solution, and 4 c.c. of caustic potash, 1:1. The stopper was inserted and the Lunge nitrometer was filled with water. The level in the two tubes was adjusted by closing the stop cock D, and turning the stop cock E in such a position that the connection was made with the outside atmosphere and the nitrometer ; and the level in the nitrometer tube is raised zero by raising the level in the levelling tube F. E was then turned so that the connection was between the outside atmosphere and the reaction vessel A. D was then opened and allowed to remain in that position for about five minutes so that A should come to the atmospheric pressure. E was then turned so that the connection was made between the nitrometer and the reaction vessel. The vessel A was given a rotatory motion and gradually tipped on one side to mix the contents of the vessel B with contents of the vessel A. Gentle shaking is continued till the level of water remains constant. Oxygen evolved was collected at a low pressure. The reaction is

complete in half a minute and after a minute's cooling the level of the tube was adjusted again and the volume of oxygen collected was noted, and the amount of SOOH calculated in terms of oxygen. Several such readings were taken and the mean results are tabulated below.

Gas Volumetric Estimation of SOOH in Organic Sulphinic Acids.

Sulphinic Acid.	Amount of acid (in gm.)	Vol. of O₂ liberated at N.T.P. (in c.c.).	% SOOH found (in gms).	% SO₂H cal. (in gms.).	Error.
Benzene sulphinic Acid	0·249	19·56	45·58	45·77	—·19
p-Toluene sulphinic acid ...	0·232	16·70	41·78	41·67	+·11
p-Chloro-benzene sulphinic acid ...	0·294	18·63	36·78	36·83	—·05
p-Dichloro-benzene sulphinic acid ...	0·252	13·36	30·77	30·80	—·03
p-Bromobenzene sulphinic acid ...	0·333	16·86	29·39	29·41	—·02
p-Dibromo-benzene sulphinic acid ...	0·284	10·58	21·62	21·67	—·05
6 :3-Chloro-nitro-benzene sulphinic acid.	0·310	15·67	29·34	29·34	·00
p-Nitro-toluene sulphinic acid ...	0·295	16·42	32·29	32·33	—·04
p-Anisole sulphinic acid ...	0·324	21·06	37·72	37·79	—·07
p-Phenetole sulphinic acid ...	0·321	19·35	34·98	34·94	+·04
Sulphino-acetanilide	0·281	15·89	32·83	32·66	+·17
p-Sulphino-phenyl acetic acid ...	0·282	31·86	32·27	32·50	—·23
4-Sulphino-cinnamic acid ...	0·269	28·86	30·59	30·66	—·07
Sulphino-benzoic acid	0·231	27·78	34·90	34·94	—·04
p-Sulphino-salicylic acid ...	0·241	26·74	32·21	32·18	+·03
p-Methoxy tolyl sulphinic acid ...	0·265	15·95	34·98	34·94	—·01
Guaiacol sulphinic acid ...	0·275	16·39	34·59	34·57	+·02
Naphthalene sulphinic acid ...	0·306	17·70	33·57	33·86	—·29
m-Benzene disulphinic acid ...	0·263	29·32	63·52	63·10	+·42

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Photobromination of *m*-Nitrobenzylidene Malonic Ester. Part I.

By Jnanendra Chandra Ghosh and Kalipada Basu.

The photobromination of *m*-nitrobenzylidene malonic ester does not proceed to completion. The reaction is a reversible one, and depending on the intensity of incident light we obtain photo-chemical stationary state.

$$NO_2C_6H_4 \quad \qquad COOC_2H_5$$
$$ >C=C< +Br_2 \rightleftharpoons$$
$$H \qquad\qquad COOC_2H_5$$

$$NO_2C_6H_4 \qquad\qquad COOC_2H_5$$
$$ \geq C-C< $$
$$H \qquad | \quad | \quad COOC_2H_5$$
$$ Br \; Br$$
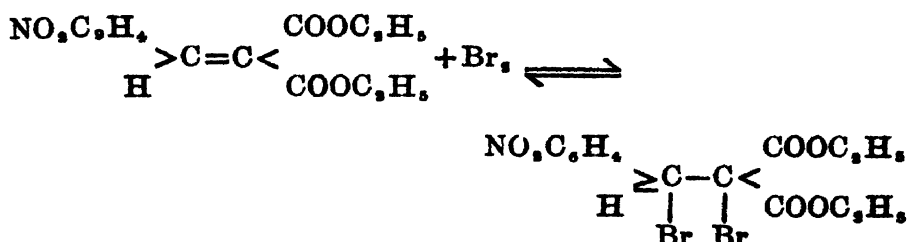
A reaction which is very similar to the present one is the photobromination of α-phenylcinnamic nitrile. This reaction has been investigated by Plotnikow (*Zeit. wiss. Photographie*, 1919, **19**, 1) and more recently by Berthoud who gives only a summary of his results in the *Transactions of the Faraday Society*, February, 1926.

The velocity of bromination of *m*-nitrobenzylidene malonic ester in the dark is practically negligible, in carbon tetrachloride as solvent. The reaction, however, proceeds fairly quickly under strong illumination, the extent of bromination increasing with increase in the intensity of illumination. In this paper the results of a quantitative study of this reaction in solutions of carbon tetrachloride will be described.

Experimental.

A pointolite lamp of 1000 C.P. maintained with a current of 6 amperes kept constant by means of a sliding resistance was used as the source of light. A parallel beam was obtained by placing a convex lens at its focal distance from the source. The light before falling on the reaction vessel passed through filter cells (2·5 c.m. thick) containing copper sulphate (16 g. per 100 c.c.) and methyl green solutions whereby light of mean wave-length 488·5 μμ was obtained.

The intensity of the light was measured by means of a Johansen thermopile and low resistance galvanometer calibrated with a Hefner lamp using Gerlach's values. The reaction vessel of plane-parallel glass slides (1·5×1·×1·5 cm.) with a close fitting glass stopper at the top was kept inside a double jacketed copper box with an opening in front. The copper box was maintained at a constant temperature by circulating water from a thermostat by means of a pump. The intensity of illumination was varied by using lenses of different focal lengths.

The ester was prepared in the laboratory by condensation of *n*-nitrobenzaldehyde and malonic ester (Ruhemann, *J. Chem. Soc.*, 1903, **83**, 723) and crystallised twice; m.p. 76°. The bromine was frozen out and then distilled. Merck's reagent carbon tetrachloride was further purified in the laboratory.

One c.c. of the reaction mixture was withdrawn from time to time by means of a pipette and titrated with N/500 thiosulphate solution.

Table I represents the results of experiments with a 500 C.P. pointolite lamp, a lens of 15 cm. focal length and a filter of N/15 copper sulphate solution, 2·5 cm. thick. This filter cuts off the infra-red and a large part of the red light.

TABLE I.

Temperature 32°.

Initial conc. of ester : gm. mol./litre.	Initial conc. of bromine : gm. mol./litre.	Equilibrium conc. of bromine : gm. mol./litre.	Dibromide / Bromine × Ester
0·0067	0·0070	0·0038	230
0·0050	0·0051	0·0030	233
0·0133	0·00715	0·0021	290
0·0100	0·0051	0·0018	270
			Mean 264

Experiments were then carried out with the 1000 C.P. point-o-lite lamp in approximately monochromatic light using copper sulphate and methyl green filters. The mean wave-length of the incident radiation was 468·5μμ. Tables II and III represent the results.

TABLE II.

Intensity of light (488·5 $\mu\mu$) 2·5 Hefners-at-100 cm.

Temperature 32°.

Initial conc. of ester : gm. mol./litre.	Initial conc. of bromine : gm. mol./litre.	Equilibrium conc. of bromine : gm. mol./litre.	Dibromide / Bromine × Ester
0·0100	0·00980	0·0048	210
0·0067	0·00655	0·00855	280
0·0050	0·00525	0·00325	210
0·0050	0·00965	0·00655	250
			Mean 285

TABLE III.

Intensity of light (488·5$\mu\mu$) 6 Hefners-at-100 cm.

Temperature 32°.

Initial conc. of ester : gm. mol./litre.	Initial con. of bromine : gm. mol./litre.	Equilibrium con. of bromine : gm. mol./litre.	Dibromide / Bromine × Ester
0·010	0·00995	0·00410	344
0·0067	0·00665	0·00300	399
0·0067	0·00880	0·00435	330
0·0133	0·0066	0·00180	314
			Mean 345

Experiments were then carried out to note the effect of temperature on the equilibrium. Table IV gives the results.

Initial conc. of ester : gm. mol./litre.	Initial conc. of bromine : gm. mol./litre.	Equilibrium conc. of bromine : gm. mol./litre.	Dibromide / Bromine × Ester
0·010	0·010	0·00435	298
0·0067	0·00855	0·00475	276
0·0133	0·0067	0·0020	279

Discussion of Results on Photochemical Stationary State.

In the bromination of a-phenyl cinnamic nitrile, Plotnikow found that the equilibrium constant K was given by the empirical relation,

$$K = \frac{I\left[1-e^{-\epsilon d(a-x)}\right]^2[b-x]}{}$$

where $I =$ Intensity of incident light,

　$\epsilon =$ molecular extinction coefficient.

a and b are the initial concentrations of bromine and acceptor,

$x =$ the concentration of dibromide formed.

This equation is far less rational than the following expression developed in his *Lehrbuch* (pp. 251, 253) for similar reactions.

$$K = \frac{I^2\left[1-e^{-\epsilon d(a-x)}\right]^2(b-x)}{x}$$

Berthoud on the other hand found that the equilibrium in the above reaction is independent of the intensity of light and the constant is given by the equation,

$$K = \frac{\{k_1[A] + k_2[ABr_2]\}[Br_2]}{[ABr_2]}$$

When ABr_2 is small compared with A, we obtain the expression for the ordinary law of mass action,

$$K = \frac{[A]\,[Br_2]}{[ABr_2]}$$

It will be seen from Tables I, II, III, and IV, that for the photobromination of m-nitrobenzylidene malonic ester, the ratio $[ABr_2]/[A]\,[Br_2]$ given in the fourth column is approximately constant. But unlike Berthoud's results on the bromination of the nitrile, the equilibrium constant in this case changes with variation in the intensity of light.

A comparison of Tables II and III brings out the interesting fact that the ratio of the equilibrium constants 235/345 or 0·68 is equal to the square root of the ratio of incident intensities $\sqrt{2\cdot56/6} = \cdot66$. This is an important relation and as will be shown later it furnishes a clue as regards the mechanism of reaction. It was also noticed that when once photochemical equilibrium has been attained under a definite intensity of illumination, the equilibrium is not in the least shifted, if the reacting system is quickly transferred to darkness. It is quite clear, therefore, that both the bromination of m-nitrobenzylidene malonic ester and the decomposition of its dibromide can only take place under the stimulus of light.

From Tables III and IV it will be also seen that the equilibrium constant is only slightly affected by changes in temperature. An increase in temperature, however, favours an increase in the concentration of the dibromide—a result which is the reverse of Plotnikow's observation on the nitrile.

Experiments on the Rate of Bromination.

Since the equilibrium is given by $\dfrac{\text{Dibromide}}{\text{Br} \times \text{Ester}}$, the velocity of bromination should be given by

$$\frac{dx}{dt} = k_1(a-x)(b-x) - k_2 x$$ where a and b represent the initial concentrations of ester and bromine respectively and x the concentration of dibromide formed.

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Now when $a=b$

$$\frac{dx}{dt} = k_1(a-x)^2 - k_2 x$$

Integration of this equation gives

$$k_1 = \frac{1}{t}\left\{ \frac{1}{2\sqrt{\lambda(2a+\lambda)}}\left[\log\frac{a+\lambda-x+\sqrt{\lambda(2a+\lambda)}}{a+\lambda-x-\sqrt{\lambda(2a+\lambda)}} \right.\right.$$

$$\left.\left. - \log\frac{a+\lambda+\sqrt{\lambda(2a+\lambda)}}{a+\lambda-\sqrt{\lambda(2a+\lambda)}} \right] \right.$$

where $\frac{1}{2\lambda} = \frac{k_1}{k_2} = K.$

Putting a' for $a+\lambda+\sqrt{\lambda(2a+\lambda)}$

and b' for $a+\lambda-\sqrt{\lambda(2a+\lambda)}$,

$$k_1 = \frac{1}{t}\cdot\frac{1}{a'-b'}\left[\log\frac{b'}{b'-x} - \log\frac{a'}{a'-x} \right]$$

When a is different from b, the expression for k_1 becomes more complicated. Tables V—VII give the results of experiments on the rate of bromination. Intensity of the incident radiation (488·5 $\mu\mu$) was 6 Hefners-at-100 cm. The time is expressed in minutes.

TABLE V.

Conc. of ester—0·010 M.   Bromine—0·00985 M

$$\frac{1}{2\lambda} = 344, \text{ Temperature } 38°.$$

Time in mins.	N/500 Bromine		
9	9·85 c. c.	...	
20	8·75	0·642	
50	7·3	0·745	
80	6·6	0·681	Mean 0·682
125	5·8	0·660	

TABLE VI.

Conc. of ester—·0067 M   Conc. of bromine—0·00665 M

$$\frac{1}{2\lambda} = 344.$$ Temperature 32°.

Time in mins.	N/500 Bromine	k	
0	6·65 c. c.	...	
20	6·1	0·681	
55	5·3	0·703	Mean 0·675
140	4·4	0·640	

TABLE VII.

Conc. of ester—0·010 M   Conc. of bromine—0·0103 M

$$\frac{1}{2\lambda} = 298.$$ Temperature 25·5°.

Time in mins.	N/500 Bromine	k	
0	10·3 c. c.	...	
25	9·6	0·294	
55	8·9	0·294	
95	8·1	0·304	Mean 0·299
135	7·5	0·304	

Tables V and VI give the same value of k, showing that the velocity of the direct reaction is not appreciably affected by the ester, bromine or dibromide.

Temperature Coefficient of k_1 and k_2.

Comparison of Tables V and VII shows that the temperature coefficient of k_1 is about 3·5 ($2 \cdot 3^{10/6 \cdot 5}$) for 10°C. We can now calculate the temperature coefficient of k_2. Let x be the temperature coefficient of k_2 for 6·5°C (32—25·5°).

Now at $25 \cdot 5°$, the equilibrium constant $K_1 = \dfrac{k_1}{k_2}$

$$= 280 \ (vide \ \text{Table IV}).$$

K_2, the equilibrium constant at $32 \cdot 5°C = 345 \ (vide \ \text{Table III}).$

Again,

$$K_2 = \frac{k_1 \text{ at } 25 \cdot 5° \times 2 \cdot 3}{k_2 \text{ at } 25 \cdot 5° \times x}$$

$$= K_1 \times \frac{2 \cdot 3}{x}$$

or $345 = \dfrac{280 \times 2 \cdot 3}{x}$

or $x = 1 \cdot 8.$

Therefore, the temperature coefficient of k_2 for $10°C$

$= 1 \cdot 8^{10/6 \cdot 5} = 2 \cdot 4$—a value less than that for k_1.

Application of Einstein's Law of Photo-chemical Equivalence.

Although this reaction is a reversible one, during the first twenty or 25 minutes the effect of the reverse reaction will not be very great and we can approximately calculate the quantum efficiency. Thus taking the results in Tables V and VII where the intensity of incident radiation ($488 \cdot 5 \ \mu\mu$) was six Hefners-at-100 cm.,

Number of quanta absorbed per sq. cm. per second

$$= 6 \times 900 \times \left(\frac{488 \times 10^{-7}}{3 \times 10^{10}}\right) \times \left(\frac{1}{6 \cdot 5 \times 10^{-27}}\right)$$

$= 13 \cdot 5 \times 10^{14}$ quanta per sq. cm. per second.

(i) Taking the results in Table V where the change is $1 \cdot 1$ c.c. N/500 Br per c.c. in the first twenty minutes we have

Number of gm. mols transformed per sq. cm. per second × depth of reaction vessel (1·5 cm.)

$$\frac{1\cdot1}{1000 \times 1000} \times \frac{1}{20 \times 60} \times 1\cdot5 \text{ gm. mols per sec.}$$

$$= 18\cdot8 \times 10^{-10} \text{ gm. mols per sec.}$$

$$= 18\cdot8 \times 10^{-10} \times 6\cdot1 \times 10^{23} \text{ mols per sec.}$$

$$= 8\cdot42 \times 10^{14} \text{ mols per sq. cm. per sec.}$$

Thus about 1·5 quanta are necessary for one molecule transformed.

(ii) Taking the results in Table VII where the change is 0·7 c.c. N/500 Br per c.c. in the first 25 minutes we have

Number of gm. mols transformed per sq. cm. per sec.

× depth of reaction vessel (1·5 cm.)

$$= \frac{\cdot7}{1000 \times 1000} \times \frac{1}{25 \times 60} \times 1\cdot5 \text{ gm. mols per sec.}$$

$$= 7 \times 10^{-10} \text{ gm. mols per sec.}$$

$$= 7 \times 10^{-10} \times 6\cdot1 \times 10^{23}$$

$$= 4\cdot27 \times 10^{14} \text{ molecules per sq. cm. per sec.}$$

Thus about 3 quanta are necessary for each molecule transformed. It is quite evident that the quantum efficiency is less than unity.

Probable Mechanism of the Photochemical Reaction between Bromine and m-Nitro-benzylidene Malonic Ester.

Any mechanism of reaction that may be proposed should be in a position to explain quantitatively the following facts :—

(a) That both the bromination and the reverse reaction are photo-chemical in nature.

(b) That the equilibrium constant $\dfrac{[\text{Dibromide}]}{[\text{Br}] \times [\text{Ester}]}$ is proportional to the square root of the intensity of incident light.

(c) That the resultant velocity is given by the equation

$$\frac{dx}{dt} = k_1 (a-x)^2 - k_2 x$$

(d) That the maximum transformation per quantum absorbed should be one molecule.

The investigations of Bodenstein and Berthoud lead to the general conclusion that the absorption of light by bromine results in the decomposition of the molecule of bromine into atoms. Recently Bernard Lewis in a note (*Nature*, April 2, 1927) has brought out evidence in favour of photochemical decomposition of hydrogen iodide into atoms of hydrogen and iodine, thus proving the untenability of the interpretation given by Stern and Volmar on the basis of excited molecules produced by the absorption of a quantum of light. We shall assume that the bromine atoms are the active agents in this photochemical reaction. Bonhoeffer (*Zeit. physikal. Chem.*, 1925, **116**, 391 ; 1926, **119**, 385) finds that atomic hydrogen represents a metastable condition, whose life is of the order of 0·3 sec. under favourable conditions. This relatively long life is explained by assuming that two atoms cannot spontaneously recombine to form a molecule. In order that they may combine and lose the energy of recombination some third body must be present to take up this energy. This hypothesis of Bonhoeffer may be extended to the process of photobromination in solution. The concentration of bromine atoms at a steady state in solution will be determined by its rate of formation due to light absorbed by bromine molecules and the rate of recombination of bromine atoms in presence of a third body—mostly molecules of solvent under favourable conditions.

$$\frac{d[\mathrm{Br}]}{dt} = k_1 I \text{ (absorbed)} \qquad \dots \quad (1)$$

$$-\frac{d[\mathrm{Br}]}{dt} = k_2 [\mathrm{Br}] [\mathrm{Br}] [S] \text{ where } S \text{ is the con. of solvent}$$

molecules.

Since S is constant, at the steady state

$$[\mathrm{Br}] = \sqrt{\frac{k_1}{k_2} \frac{I}{S}} = k \sqrt{I} \qquad \dots \quad (2)$$

Some of the bromine atoms may, however, combine in a three body collision where the third body may be the ester molecule or the bromine molecule. We may now postulate tentatively the following mechanism for the reaction studied here :

$$[Br] + [Br[+ [A] = A \text{ (excited)} + Br,$$
$$\text{where } A \text{ denotes the ester.}$$

$$[Br] + [Br] + [Br,] = Br, \text{ (excited)} + Br,$$

$$A \text{ (excited)} + Br, \rightleftharpoons ABr,$$

$$Br, \text{ (excited)} + A \rightleftharpoons A Br,$$
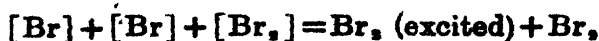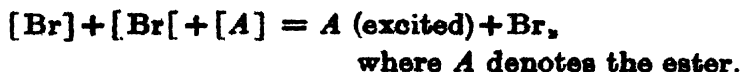
The effect is the same as if the following reaction takes place

$$Br + Br + A + Br, \rightleftharpoons ABr, + Br, \qquad \dots \quad (3)$$

and hence the rate of formation of the ester-dibromide is given by

$$k_s [Br] [Br] [A] [Br,]$$

$$= k_s \sqrt{I} \; \sqrt{I} \; [A] \; [Br,]$$

$$= k_s \; I \; (a-x) \; (b-x) \qquad \dots \quad (4)$$

where a is the initial conc. of ester and b the initial conc. of bromine and x the concentration of dibromide.

The reverse reaction

$$ABr, \rightleftharpoons A + Br,$$
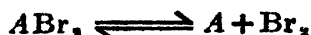
can only take place when the dibromide molecule collides with an atom of bromine. The velocity of this photo-decomposition is therefore given by the equation

$$k_6 [X] [Br] = k_6 \sqrt{I} \; [X] \qquad \dots \quad (5)$$

The observed velocity of photo-bromination is the difference between these two velocities, and has the value

$$k_s I (a-x) (b-x) - k_6 \sqrt{I} [X] \qquad \dots \quad (6)$$

At the steady state when the equilibrium is reached,
Equation (6) = 0 and we have

$$\frac{X}{(a-x)(b-x)} = \frac{k_s I}{k_6 \sqrt{I}} = \frac{k_s}{k} \sqrt{I} \qquad \dots \quad (7)$$

The mechanism proposed above also indicates that for every quantum of light absorbed the number of dibromide molecules that can be produced according to equation (3) cannot exceed unity.

We have thus been able to explain the experimental observations on the basis of a mechanism which is at least not more complicated than what obtains in this field.

Our best thanks are due to Mr. Sisir Kumar Ghosh, M.Sc. for carrying out a large number of preliminary experiments.

The Effect of the Addition of some Alkaloids on the Rate of Solution of Iron in Dilute Hydrochloric Acid. Part II. The Effect of Nicotine, Narcotine and Gelatine and the Fall in *E. M. F.* produced in the Iron in Presence of Brucine.

By M. B. Rane.

In a previous communication on the subject by Rane and Prasad (*J. Phys. Chem.*, 1925, **29**, 249), it was pointed out that the rate of solution of iron in hydrochloric acid increases as the reaction progresses and that the alkaloids have a considerable inhibiting effect on the rate of solution. It was there suggested that the rise in the rate of solution was perhaps due to the increased surface presented by the iron due to its becoming more and more porous with the progress of the reaction. The inhibition produced by the alkaloids was also supposed to be a phenomenon akin to passivity. In the present communication, the work has been extended to two other alkaloids and to some other substances and an attempt is made to examine the assumptions made about the increase in the rate and the inhibition. The experiments were conducted with the same iron wire and in the same apparatus as stated in Part I (*loc. cit.*).

Changes in the Surface of the Iron.

The iron wire in the experiments in question, when subjected to the action of acids becomes porous and the surface consequently becomes so irregular that direct measurement of the surface from time to time by a physical method becomes impossible. A chemical method had therefore to be resorted to. It is a well known fact that iron precipitates copper from a solution of copper sulphate. The following experiments show that the amount of copper precipitated is nearly proportional to the amount of the surface of the iron exposed to the action. Coils of iron wire of different lengths were introduced into copper sulphate solution and kept there for ten

14

minutes. The amount of copper precipitated was then determined by finding out the amount of copper left in solution by the method of Ian William (*J. Chem. Soc.*, 1922, **121**, 358). The results are given in Table I.

TABLE I.

Time of reaction 10 minutes; Iron wire, diam. ·0927 cm.; Copper sulphate solution=5 gm. $CuSO_4$, $5H_2O$ in 100 c.c.

Length of iron wire. (cm.)	Volume of copper sulphate solution. (c.c.)	Grams of copper precipitated.
10	50	·0013
20	50	·0028
30	50	·0039
50	50	·0071

The amount of copper precipitated is nearly proportional to the amount of surface exposed. It is clear, therefore, that if by exposing the iron wire to the action of hydrochloric acid it becomes more porous and forms greater surface it should deposit more copper than iron wire not so exposed, and that the quantity so deposited should give a rough measure of the new surface formed. The results given in Table II however do not show this to be true.

TABLE II.

Strength of Copper Sulphate Solution=0·5 per cent.

Wire No.	Condition of the wire 50 cm. long.	Amount of Cu deposited in 10 min. (gm.)	Rate of solution in N/1HCl in c.c. of hydrogen in 20 minutes.
1	Iron wire fresh	·0071	18·68
2	Iron after dipping in HCl for 1 hour	·0061	30·09
3	Iron after dipping for 2 hours ...	·0051	37·54
4	Iron after dipping for 3 hours ...	·0043	53·52

It is seen from the above that the rate of solution rises with length of exposure of the iron to the acid and becomes nearly three times at the end of the third hour—whereas the amount of copper precipitated by the irons so exposed gets less and less. It was, however, observed in the case of wire No. 1 that the deposition of copper went on quite regularly and uniformly, whereas in the case of Nos. 2, 3 and 4 the deposition was incoherent and was accompanied by evolution of gas which was found to be hydrogen. This hydrogen which must have been adsorbed in the nascent condition while the iron was dissolving in hydrochloric acid (Friend, " Text-book of Inorganic Chemistry," Vol. IX, Part II, p. 44) must be hindering the free access of copper ions to the surface of the iron and might be responsible for not allowing copper to be precipitated in proportion to the new surface formed. To expel this adsorbed hydrogen the iron wire after exposure to hydrochloric acid for two hours was kept for about 15 minutes in vacuum in the one case, was boiled with distilled air-free water in the second case and boiled with absolute alcohol in the third. but in no case was the subsequent precipitation of copper from copper sulphate solution proportional to the supposed increase in the surface of the iron, though the amount of precipitate was slightly more than before. The adsorbed hydrogen therefore could not be got rid of by the above methods and unless some new modifications·are introduced this method for measuring the irregular surface would not do.

Influence of Iron Salt as a Catalyst.

During the course of discussion on Part I of the communication in the Indian Science Congress, it was suggested that the increased rate of solution might be due to the catalytic influence of the iron salt formed in the reaction. The following experiments, however, do not justify that suggestion. The successive rates of solution of iron wire (A) about 50 cm. in length were determined as before for two hours, then the wire was removed, washed with distilled water and introduced into fresh acid, and a new iron wire (B) of the same length was introduced into the acid which had already acted for two hours. The new rates of solution were then determined as before and it was found that the new wire (B) began to dissolve as if fresh

acid alone was used, that is, it began to dissolve with the usual low initial rate which gradually began to increase showing that the dissolved iron salt had no catalytic effect—whereas the wire (A) previously dipped in the acid for two hours began to dissolve in the fresh acid at a higher rate—rate nearly the same at which it was dissolving when it was removed from the old acid. This makes it clear that the increase in the rate of solution is not due to any catalytic influence of the salts formed in the solution but to something in the wire itself,—may be the increased surface. The strength of the acid was, of course, kept constant by the addition of strong acid from outside from time to time. The results are shown in Table III.

TABLE III.

300 c.c. N/1 HCl ; Temp. 45°.

Time in minutes.	Volume of gas evol-ved per 20 minutes at N. T. P. (c.c.)	Time in minutes.	Volume of gas evolved per 20 minutes at N.T.P. (c.c.)

Wire A.

0— 20	24·9
20— 40	45·3
40— 60	55·5
60— 80	54·4
80—100	57·7
100—120	,, ,,

The iron wire (A) is removed and fresh wire (B) of the same length introduced in the solution now containing the iron salt.

0—20	29·3
20—40	43·8
40—60	47·7

The iron wire (A) introduced in fresh N/1 HCl after two hours action in N/1HCl.

0—20	50·2
20—40	53·9
40—60	

Influence of the Capillaries Formed.

It appears that the rapid increase in the rate might be due to the capillaries produced in the iron. This view is supported by the

observation of McCullock (*J. Amer. Chem. Soc.*, 1925, 47, 1940). He has shown that if a tightly fitting rubber tubing is slipped on the middle of an iron rod leaving both ends free and the rod then dipped in hydrochloric acid for a week or so, curiously enough the rod is corroded and eaten up more under the rubber tubing than in the freely exposed part. Further in another interesting experiment he has shown that the above effect can be observed visually. A glass slide is attached to a flat piece of iron and then dipped in dilute acid. Beneath the glass the capillary space is seen to be largely filled with greatly flattened bubbles, the boundaries of which are in slow but constant motion. The bubbles go on extending till the edge is reached when they break suddenly and small bubbles are ejected with violence. It is seen that small bubbles of gas sink into the capillaries formed during the action of acid upon the metal, the bubbles increase in size and become flattened or lengthened. They break off suddenly at the edges and the pressure being released on the sides of the capillaries, the corrosion takes place faster there than at the smooth surface. This is probably also the explanation of the increased rate of solution of iron in acids in our experiments. As time advances the metal becomes more and more porous or interspersed with small capillaries all round, and these make the action more and more brisk. Even on theoretical grounds it has been shown by J. J. Thomson that capillarity tends to increase the chemical action (Rideal and Taylor, "Catalysis in Theory and Practice," pp. 46-48).

The Inhibiting Effect due to added Substances.

The experiments mentioned in the previous communication have now been extended to alkaloids, nicotine and narcotine. It was believed that the inhibition was due to the poisonous substances alone, but it has been found that gelatine also exercises a similar inhibiting effect. No such inhibiting effect, however, was found to be exercised by cane sugar, glucose, aniline hydrochloride, phenol, cresol, nitrobenzene and phenylene diamine. In Tables IV, V and VI are given the results, obtained with nicotine, narcotine and gelatine using 50 cm. of iron wire and 300 c.c. of N/1HCl at 45°.

TABLE IV.

Effect of Nicotine on the Rate of Solution of Iron in N/1HCl.

Time (minutes).	Volume of gas evolved on the addition of the following quantities initially.				
	Without any alkaloid.	0·02 g.	0·01 g.	0·002 g.	0·001 g.
	c.c.	c.c.	c.c.	c.c.	c.c.
0— 20 ...	18·7	0·50	3·1	5·5	5·8
20— 40 ...	23·6	2·7	5·5	11·4	10·3
40— 60 ...	27·1	6·2	9·5	16·7	21·0
60— 80 ...	30·1	9·1	12·4	23·0	29·7
80—100 ...	31·4	11·4	16·0	29·1	34·7
100—120 ...	35·8	13·8	19·3	38·2	33·7
120—140 ...	37·5	15·6	19·5	31·6	32·2
140—160 ...	41·2	16·9	21·0	32·7	35·3
160—180 ...	45·7	17·5	22·9	33·8	37·5
180—200 ...	53·5	19·1	25·2	35·5	38·4
200—220 ...	58·2	19·0	27·3	36·9	42·9
220—240 ...	63·2	18·8	29·2	40·0	46·8

TABLE V.

Effect of Narcotine on the Rate of Solution of Iron in N/1HCl.

Time (minutes).	Volume of gas evolved on the addition of the following quantities initially.			
	Without any alkaloid.	0·02 g.	·01 g.	·002 g.
	c.c.	c.c.	c.c.	c.c.
0—20 ...	18·7	0·4	1·1	5·5
20—40 ...	23·6	2·0	4·2	12·9
40—60 ...	27·1	4·1	6·9	18·2
60—80 ...	30·1	6·7	11·9	22·0
80—100 ...	31·4	6·3	13·4	23·4
100—120 ...	35·8	7·8	14·5	26·4
120—140 ...	37·5	8·3	15·8	27·4
140—160 ...	41·2	9·3	16·0	29·7
160—180 ...	45·7	9·8	17·4	31·4
180—200 ...	53·5	9·9	18·0	33·0
200—220 ...	58·2	9·7	17·9	33·9
220—240 ...	63·2	10·8	18·1	34·0

TABLE VI.

Effect of Gelatine on the Rate of Solution of Iron in N/1HCl.

Time (minutes).	Volume of gas evolved on the addition of the following quantities initially.				
	Without any alkaloid.	0·04 g.	·004 g.	·0004 g.	·0002 g.
	c.c.	c.c.	c.c.	c.c.	c.c.
0— 20	18·7	2·0	4·2	6·3	7·7
20— 40	23·6	4·3	5·1	14·7	16·5
40— 60	27·1	7·5	8·7	21·5	23·5
60— 80	30·1	9·4	11·6	21·4	29·2
80—100	31·4	11·3	14·3	31·8	34·6
100—120	35·8	11·5	17·1	36·2	25·0
120—140	37·5	11·7	18·1	38·0	36·8
140—160	41·2	10·8	20·0	36·9	38·1
160—180	45·7	10·3	20·6	42·3	42·3
180—200	53·5	10·7	23·2	39·6	46·7
200—220	58·2	10·1	26·3	38·9	51·2
220—240	63·2	9·23	28·1	43·6	56·1

The Fall in the E.M.F. of the Iron under the Influence of Brucine.

It is known that when iron is dipped in a passivifying agent such as chromic or nitric acid, there is a change produced in the iron and the iron becomes more noble or in other words its *E.M.F.* falls. Experiments were therefore tried to find out if there was any fall in the *E. M. F.* of the iron in presence of varying quantities of the alkaloid brucine. Two sets of experiments were made. One set of experiments was made with iron wire dissolving in N/1HCl, with and without the addition of small quantities of brucine and in another set a similar iron wire and N/1 ferrous sulphate were used. The potentiometer was a Leeds and Northrup one and in both sets of experiments a normal calomel electrode was used as the other electrode of the cell. The *E.M.F.* measurements given below were reproducible with an error of 0·002 volt, and represent the mean of five readings taken during the first five minutes.

TABLE VII.

Cell   E.M.F. *in Volts.*

Fe	N/1HCl		KCl saturated		Hg$_2$Cl$_2$	Hg	
					N/1KCl		0·556

The *E.M.F.* and the fall in the *E.M.F.* when brucine in varying quantities
is added to the N/1HCl.

N/1HCl containing					*E.M.F.*	Fall in the *E.M.F.*
0·000 g. brucine	...	...	...		0·556	
0·00049 g. brucine in 100 c.c. HCl	...	...		0·551	0·005
0·00098 ,, ,,	...	...		0·548	0·008
0·00195 ,, ,,	...	...		0·547	0·009
0·0039 ,, ,,	...	...		not determined	not determined
0·00781 ,, ,,	...	...		0·535	0·021
0·0156 ,, ,,	...	...		not determined	not determined
0·03125 ,, ,,	..	...		0·527	0·029
0·0625 ,, ,,	...	...		0·522	0·034
0·125 ,, ,,	...	...		0·518	0·038
0·250 ,, ,,	...	...		0·514	0·042
0·500 ,, ,,	...	...		0·488	0·068
1·000 ,, ,,	...	...		0·486	0·070
2·00 ,, ,,	...	...		0·483	0·073

TABLE VIII.

Cell   E.M.F. *in Volts.*

Fe	N/1FeSO$_4$		KCl saturated		Hg$_2$Cl$_2$	Hg	
					N/1KCl		0·633

The *E.M.F.* and the fall in the *E.M.F.* when brucine in varying quantities
was added to the N/1FeSO$_4$.

N/1FeSO$_4$ containing					*E.M.F.*	Fall in the *E.M.F.*
0·00 gram brucine	...	...	...		0·633	
0·125 g. brucine in 100 c.c. FeSO$_4$		...		0·606	0·027
0·250 ,, ,,	...	...		0·597	0·036
0·500 ,, ,,	...	...		0·574	0·059

The results obtained show that in presence of brucine the iron dissolving in N/1HCl becomes more and more passive as we increase the concentration of the alkaloid up to a certain limit, with iron wire in contact with N/1FeSO₄ the results obtained were similar.

Summary.

The increase in the rate of solution of iron in hydrochloric acid as the reaction progresses is ascribed chiefly to the capillaries formed in the iron and also partly to the increased surface produced. The action of hydrochloric acid on iron is inhibited not only by alkaloids but by gelatine as well. The $E. M. F.$ of the iron in contact with N/1HCl as also with N/1FeSO₄ falls in presence of small quantities of alkaloids—a phenomena akin to that of passivity of iron.

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Organo-antimony Compounds.

Part I.

By Sudhir Chandra Niyogy.

The object of this investigation was to find the relation, if any, that exists between the physiological action and chemical composition of the halogen substitution products of sodium p-acetylaminophenyl stibinate.

The first compound of this type, sodium 4-acetylamino-3-chlorophenyl stibinate (known in the trade as Von Heyden's 471) had already been described by Brahmachari and Das (*Ind. J. Med. Research*, **13**, 17). Previously this compound was largly used for the treatment of kala-azar but has now been superseded by ureastibamine (Brahmachari, *Ind. J. Med. Research*, 1922, **10**, 492), the carbamino derivative of the ammonium salt of p-aminophenyl stibinic acid. A study of the action of these two antimony compounds brings out a remarkable fact. According to opinion of medical profession, Von Heyden's 471 and ureastibamine are equally active at first after but a time the action of Von Heyden's preparation begins perceptibly to fall off, while that of ureastibamine continues the same as before (private communication). The conclusion that can be drawn from this difference in the activity appears to be that after a patient has been given a certain number of injections of Von Heyden's preparation, the system becomes tolerant to it and so no further improvement takes place. This led the author to prepare other halogen substituted derivatives in the hope that the inefficiency of Von Heyden's compound may be removed and the medical profession may be provided with a suitable and stable substance (ureastibamine is very unstable) for combating kala-azar.

Brahmachari (*loc. cit.*) described the preparation and properties of some derivatives of p-aminophenyl stibinic acid ; Macallum (*J. Soc. Chem. Ind.*, 1923, **42**, 468T) described o-aminophenyl stibinic acid ; whilst recently Dunning and Reid (*J. Amer. Chem. Soc.*, 1926, **48**, 2959) described some azo-derivatives of p-aminophenyl stibinic acid ; and Schmidt (*Annalen*, 1922, **429**, 145) the preparation of p-amino-p-hydroxy-and m-nitro-phenyl stibinic acid and their salts.

The starting point was in each case p-nitraniline and the mono- and di-*ortho*-substituted halogen derivatives were prepared by the

usual methods (*Ber.*, 1874, **7**, 1564; 1882, **15**, 474; 1877, **10**, 1709 ; 1875, **8**, 143; 1878, **11**, 144; 1901, **34**, 3344; *J. Chem. Soc.*, 1908, **93**, 1773; D. R. P. 109189).

The acetylation of these compounds was carried out by Orton's method (*J. Chem. Soc.*, 1908, **93**, 1242). It was found however that mono-*ortho*-substituted amines could not be completely acetylated in the absence of sulphuric acid—an observation which disproves Orton's statement that mineral acids depress rather than accelerate the rate of acetylation of mono-*ortho*-substituted amines.

The reduction of these nitro-compounds to obtain the corresponding amines gave rise to considerable difficulty. The usual reducing agents were not quite satisfactory. The operation was successfully carried out by leading sulphuretted hydrogen into an alcoholic solution of the nitro body saturated with dry ammonia.

The preparation of the corresponding antimony compounds from these amines was found to be an extremely difficult and tedious operation. As had been stated in a previous paper (this *Journal*, 1927, **4**, 96), it was always found more satisfactory to carry out the operation by the gradual addition of caustic soda solution to a suspension in water of the additive compound of the diazo-salt with antimony trichloride. But even with this method the difficulties were numerous. In some cases the decomposition of the diazo-compound was so rapid that the product isolated was the corresponding phenol. In others again, the nitrogen evolved during the reaction formed a stiff foam which prevented thorough mixing and the yield was poor. It is essential for the success of the operation that the stirring must be very vigorous. so that the contents are always thoroughly mixed up and the decomposition of the diazo-compound is not localised.

The physiological action of these antimony compounds is now being investigated.

EXPERIMENTAL.

2-*Bromo-4-nitraniline*.—*p*-Nitranniline (10 g.) was dissolved in glacial acetic acid (150 c.c.) with warming. The solution was then cooled to room temperature. Bromine (12 g.) in acetic acid was slowly added to the solution of nitraniline with stirring. The absorption of bromine was very rapid. Towards the end, a yellowish white precipitate separated and hydrobromic acid was evolved. The reaction mixture was then heated on a water-bath for about 30

minutes and then filtered off and washed thoroughly with water; m.p. 100·2°. Yield—14 gm. (The m.p. of 2-bromo-4-nitraniline, prepared by brominating p-nitroacetanilide and subsequent hydrolysis, as given in the literature is 104-105°).

2:6-*Dibromo-4-nitraniline*.—In this preparation the weight of bromine used was twice as much as in the former case and the solution of bromine was added to a hot solution of p-nitraniline in acetic acid. Yield (from 10 gm. p-nitraniline) 19 gm.; m. p. 204·5°.

2-*Iodo-4-nitraniline* and 2:6-*Di-iodo-4-nitraniline* were prepared by the method of Willgerodt and Arnold (*Ber.*, 1901, **34**, 3344). The yield was quite satisfactory.

2:6-*Dichloro-4-nitraniline*.—This compound was at first prepared according to Flürscheim's method (*J. Chem. Soc.*, 1908, **93**, 1775). But as this method required a large expenditure of acetic acid and hydrochloric acid, it was found more economical to prepare it according to the specification of Cassella & Co's patent (D. R. P. 109189), which is given out to be a process for preparing 2-chloro-4-nitraniline but was found to give 2:6-dichloro-4-nitraniline under all conditions.

Acetylation.—Orton's method (*loc.cit.*) was in each case employed, and the yields were quite satisfactory, the products being pure except in the case of 2:6-di-iodo-4-nitraniline which had to be recrystallised.

4-*Acetylamino*-3:5-*di-iodo-1-nitrobenzene*.—2:6-Di-iodo-4-nitraniline' (12 g.) was suspended in glacial acetic acid (120 c.c.) and to this was added acetic anhydride (60 c.c.). About 20-24 drops of concentrated sulphuric acid were then added to this suspension when the whole went into solution and the colour changed from yellow to light brown. This was allowed to stand for about an hour and poured into a litre of boiling water. On cooling, a light brown precipitate, m. p. 235-38°. separated. On recrystallisation from dilute alcohol the m.p. rose to 245-46°. Yield 10 gm. (Found: N, 7·04. $C_8H_6O_3N_2I_2$ requires N, 6·46 per cent.).

4-*Acetylamino*-3 *iodo-1-nitrobenzene*.—Yellowish white glistening plates, m. p. 188-89°. Yield 9·5 gm. from 10 gm. of 2-iodo-4-nitraniline. (Found: N, 9·58. $C_8H_7O_3N_2I$ requires N, 9·14 per cent.).

4-*Acetylamino*-3:5-*dichloro-aniline*.—4-Acetylamino-3:4-dichloro-1-nitrobenzene (5 g.) was dissolved in absolute alcohol with gentle warming (the volume of alcohol added must be such that the nitro compound does not separate on cooling). The alcoholic solution was then saturated with dry ammonia and treated with a slow current of hydrogen sulphide for 3 hours. The solution was then evaporated

to dryness on a water-bath and the residue extracted with water and filtered. The clear filtrate, on cooling, gave light flaky crystals, which after two recrystallisations from water melted at 209—10°. Yield 2 gm. (Found: N, 12·97. $C_8H_8ON_2Cl_2$ requires N, 12·78 per cent.).

Reduction of 4-Acetylamino-3-bromo-1-nitrobenzene.—A rather remarkable compound was isolated in the course of this reducing operation. After an alcoholic ammonia solution of 4-acetylamino-3-bromo-1-nitrobenzene had been saturated with hydrogen sulphide, the whole was evaporated to dryness on a water-bath. The residue consisted of the amino body mixed with sulphur. In some cases, it was found extremely difficult to separate this impurity. It was found that sulphur was soluble in warm pyridine and the whole of it separated upon somewhat diluting the solution. The mixture of the amine and sulphur was dissolved in pyridine and diluted with a few drops of water. A yellow precipitate separated which was filtered off and found to be sulphur. On further diluting the filtrate a yellow crystalline precipitate separated, which after recrystallisation, from pyridine melted at 270-72° whereas the m.p. of 4-acetylamino-3-bromo-aniline is 120-21°. The yellow product was found to be insoluble in common organic solvents, except pyridine and to give no diazo reaction. On analysis it was found to contain 6·5% nitrogen, the required amine containing 12·22%. The constitution of this is being investigated and will be communicated in due time.

4-Acetylamino-3-bromo-aniline.—4-Acetylamino-3-bromo-1-nitrobezene (7 g.) was dissolved in rectified spirit, cooled and liquor ammonia added and then saturated with H_2S. The residue obtained by evaporating the ammoniacal solution, after being extracted with water (twice) and on cooling in ice, did not give any precipitate. The whole was then evaporated to dryness in a vacuum desiccator when a yellow oily residue was left, easily soluble in water, alcohol and chloroform and giving the usual diazo reaction. After being left in a vacuum desiccator for a few days and on occasionally scratching with a glass rod, the oil was converted into a semi-solid mass which was then extracted with benzene. On cooling the benzene solution in ice water, white plates, m.p. 110-12°, separated. Recrystallised from benzene these had m.p. 120-21°. Yield 3 gm. (Found: N, 11·56. $C_8H_9ON_2Br$ requires N, 12·22 per cent.).

4-Acetylamino-3:5-dibromo-aniline—similar to 4-acetylamino-3:5-dicloroaniline. M.p. 285-86°. Yield (from 9 gm. nitro compound)

3·5 gm. (Found: N, 9·05. $C_8H_6ON_2Br_2$ requires N, 9·09 per cent.).

4-Acetylamino-3-iodo-aniline. — 4-Acetylamino-3-iodo-1-nitrobenzene (7 gm.) was dissolved in alcohol, saturated first with ammonia and then with sulphuretted hydrogen for 4 hours. On evaporation a yellow pasty mass was left. This was twice extracted with carbon disulphide and then with petroleum ether to remove sulphur. The residue was thrice extracted with benzene and the yellow benzene extract was decolourised by animal charcoal and filtered. On cooling in ice, a white crystalline precipitate separated, melting at 182-84°, and on crystallisation from benzene the melting point rose to 184-85°. Yield, 2·7 gm. (Found: N, 9·72. $C_8H_8ON_2I$ requires N, 10·14 per cent.).

4-*Acetylamino*-3 : 5-*di-iodo-aniline.*—The corresponding nitro compound was treated as described in the previous cases. But all attempts to purify the amine from sulphur by the method described above failed. This was, however, effected as follows: The residue obtained by evaporating the alcoholic solution was again dissolved in absolute alcohol and copper powder (prepared by precipitating copper sulphate with zinc dust) was added to it and boiled under reflux, till the red colour of metallic copper had almost disappeared. The liquid was then filtered off from the precipitated copper sulphide and evaporated on a water-bath. Twice during this operation a gelatanious precipitate of copper sulphide was formed which was removed and the whole evaporated to dryness on a water-bath. The residue, now found to be free from sulphur, was boiled with methyl alcohol with the addition of animal charcoal and filtered. The filtrate on dilution gave a precipitate melting at 240-43°. On recrystallisation from dilute methyl alcohol the melting point rose to 247-48°. Yield (from 8 gm. nitro derivative) 3 gm. (Found: N, 7·03. $C_8H_8ON_2I_2$ requires N, 6·96 per cent.).

4-*Acetylamino*-3 : 5-*dichlorophenylStibinate of Sodium.*—4-Acetylamino-3 : 5-dichloro-aniline (2·5 g.) was dissolved in water (20·c.c.) and hydrochloric acid (10 c.c.). This was cooled to 0° and diazotised. Hydrochloric acid (10 c.c.) was further added. To this diazo solution was then added antimony trichloride solution prepared by dissolving antimony trioxide (2 g.) in hydrochloric acid (20 c.c.). A yellowish white precipitate immediately separated which was left to stand in ice for half an hour with occasional stirring. The precipitate was filtered off, washed with dilute hydrochloric acid

and then with water till acid free. The moist mass was then beaten up with water cooled to 5—7° and sodium hydroxide (6 g.) dissolved in water was gradually added with vigorous stirring. The stirring was continued till the evolution of nitrogen slackened. The liquid was then filtered off and the clear filtrate acidified with dilute acetic acid when the free antimonic acid separated as a flocculent precipitate; it was washed with water till free from acid. The free acid was then suspended in water, dissolved by adding a dilute solution of sodium carbonate drop by drop and filtered off from the insoluble impurities, if any. The solution was then concentrated on a water-bath; a small quantity was removed and absolute alcohol added in large excess. But as no precipitate separated, the concentrated solution was evaporated to dryness in a vacuum desiccator and the dark coloured residue extracted with methyl alcohol, boiled with animal charcoal and filtered. On adding ether, the sodium salt of the antimonic acid separated as a faintly pink gelatanious precipitate, which was filtered off, washed with ether and finally dried in a vacuum over paraffin. (Found: N, 3·7; Sb, 29·9. $C_8H_7O_4NCl_2SbNa$ requires N, 3·5; Sb, 30·4 per cent.).

4-Acetylamino-2-phenyl stibinate of sodium was prepared as above. (Found: C, 28·64; Sb, 29·01. $C_8H_8O_4NBrSbNa$ requires C, 26·7; Sb, 29·6 per cent.).

4-Acetylamino-3 : 5-dibromophenyl stibinate of Sodium. (Found: C, 20·18 ; Sb, 25·2. $C_8H_7O_4NBr_2SbNa$ requires C, 19·8; Sb, 24·8 per cent.).

4-Acetylamino-3-iodophenyl stibinate of Sodium. (Found: C, 21·5; Sb, 25·9. $C_8H_8O_4NISbNa$ requires C, 21·2 ; Sb, 26·6 per cent.).

4-Acetylamino-3 : 5-di-iodophenyl stibinate of Sodium. (Found: C, 17·48; Sb, 21·4. $C_8H_7O_4NI_2SbNa$ requires C, 16·8; Sb, 20·5 per cent.)

Properties.—The dried sodium salts are faintly red amorphous powders, fairly soluble in water forming a red solution with a neutral reaction (litmus). On acidifying with dilute mineral acid the free acid is precipitated which can again be dissolved in dilute alkali. Some of these compounds were found to be extremely hygroscopic.

I desire to convey my thanks to Prof. H. K. Sen for the interest he has taken in the course of this work and also to Mr. K. C. Bose-Ray for having helped me in the analytical portion of the work.

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A Synthesis of Oxypalmatine: Dehydro-nor-oxy-ψ-coralydin.

By Jnanendra Nath Ráy.

The method which was successful in the synthesis of the oxy-berberine (*cf.* Perkin, Ráy and Robinson, *J. Chem. Soc.*, 1925, **127**, 740) is now applied for the preparation of oxy-palmatine. Palmatine differs from berberine in that the methylene-dioxy group of the latter is replaced by two methoxyl groups in the former alkaloid. It is clear that it should be possible to convert berberine into palmatine. Feist and Sandstede (*Arch. Pharm*, 1918, **256**, 1) failed to effect this but Späth and Lang (*Ber.*, 1921, **54**, 3064) succeeded to a limited extent in converting tetrahydroberberine into tetrahydropalmatine by heating the former with potassium hydroxide in methyl alcohol and methylating the resulting product with methyl sulphate and alkali in absence of oxygen. The doubt thrown on the synthesis of berberine by Haworth, Perkin and Rankin (*J. Chem. Soc.*, 1924, **125**, 1686) necessitated a fresh synthesis of the alkaloid. It was thought that the application of the same method would lead to a synthesis of oxypalmatine. In the present paper this is described. Recently, while this work was in progress, Späth and Quietensky (*Ber.*, 1925, **58 B**, 2267) reinvestigated their original synthesis of palmatine.*

The starting point in the present investigation has been meconine carboxylic acid (Perkin, Ráy and Robinson, *loc. cit.*) on the one hand and 3 :4-dimethoxyphenylethylamine on the other. The amide (1) prepared by condensation of the chloride of the acid with the amine

(I.)
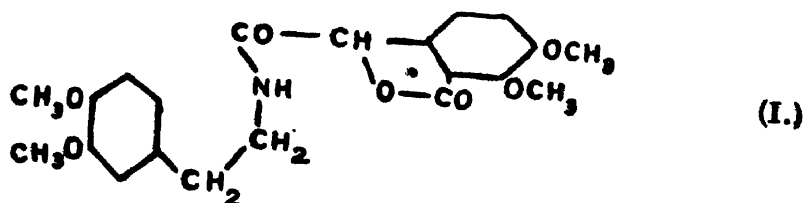
is converted into a dihydro-*iso*quinoline derivative by the prolonged

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* The present paper was read before the Indian Science Congress on the 7th January, 1927. Haworth, Koepfli and Perkin (*J. Chem. Soc.*, 1927, **131**, 548) since then obtained oxypalmatine by a totally different method. However, the substance isolated by these authors seems to be not quite pure as it melts about 11° lower than the compound described in this paper.

action of phosphoryl chloride. A small amount of a neutral product
is produced as an insoluble ocherous precipitate on decomposing the
reaction mixture with ice as in the case of the synthesis of oxy-
berberine, together with the basic dihydro-*iso*quinoline derivative
(II) as a bright yellow solution of its hydrochloride.

(II)
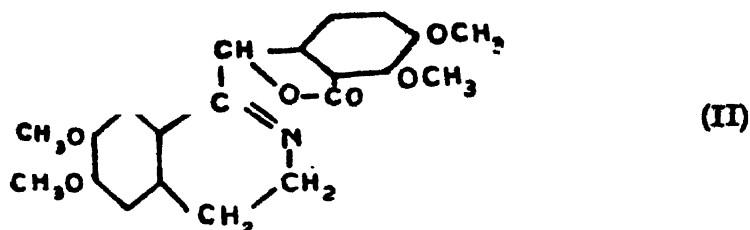
This neutral product similar to that obtained in the oxyberbe-
rine synthesis has now been purified and crystallised. This is chloro-
*nor*oxy-berberine (III) as was suggested in the former paper.
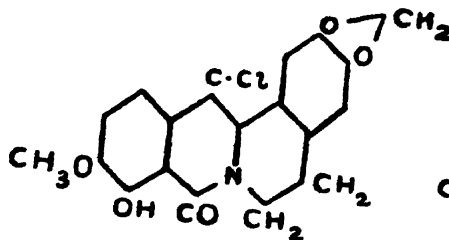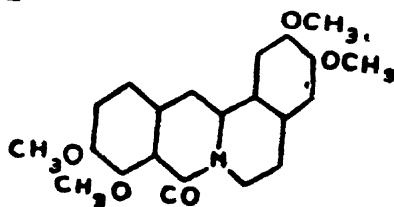
(III.)   (IV.)

The isolation of this compound suggests that a more direct syn-
thesis of palmatine is desirable than that accomplished by Späth and
Quietensky as here one of the methoxyl groups is eliminated instead
of the methylene-dioxy group which Späth and Quietensky assumed
to have been spitted off in that case. The dihydro-*iso*quinoline
compound is reduced with zinc and acetic acid when oxypalmatine
(IV) is produced. This compound melts at 194°-196° and gives
bluish-violet fluorescence in neutral organic solvents.

An examination of the formula (IV) reveals the fact that it is very
similar to a compound described by Pictet and Chou (*Ber.*, 1916,
49, 370) which they have named dehydro*nor*oxycoralydin (V) m.p.

190°. The two substances only differ in the position of the methoxyl-groups.

(V.)
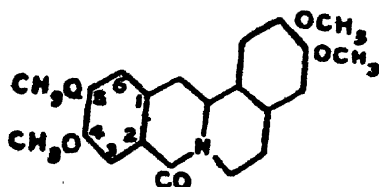
The compound (V) was synthesised by Pictet and Chou from papaverine. They condensed papaverine with methylal as in their berberine synthesis (*Ber.*, 1911, **44**, 2036) and the product on treat-, ment with alkali subsequent to oxidation by iodine is (V). It has been shown by Haworth, Perkin and Rankin (*loc. cit.*) that these condensations (*cf.* the synthesis of berberine) take place with the aid of the hydrogen atom in position 2 of the veratryl nucleus whilst Pictet and Gams claimed that the hydrogen atom in position 6 reacted. It is significant that in interpreting the very similar condensation with papaverine, Pictet and Chou use the hydrogen atom in position 2 for ring closure and not the one at 6 as in their berberine synthesis.

The purification of the base (II) has proved to be difficult as in the previous case. This seems to be due to ready oxidisability (by air in presence of alkali) observed in similar cases where a carbon atom is attached to position 1 of the *iso*quinoline nucleus (*cf.* Buck, Haworth and Perkin, *J. Chem. Soc.*, 1924, **125**, 2176). The annexed scheme will indicate the process.
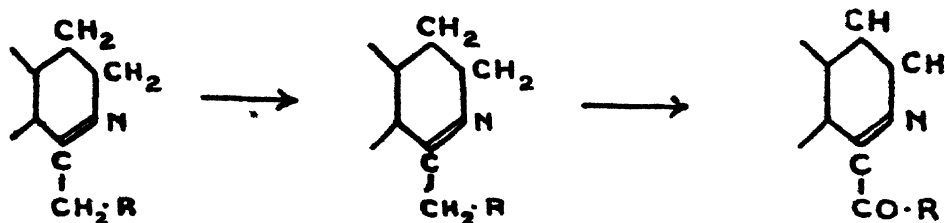
The isolation of dioxyberberine in one experiment (*cf.* Perkin, Rây and Robinson, *loc. cit.*) can be easily understood from an examination of the above scheme taken from the paper of Back, Haworth and Perkin. The dihydro-*iso*quinoline base is being prepared with the idea of oxidising it to stage (VII) and then effecting the ring closure to dioxypalmatine and dioxyberberine. This has been partially successful in the latter case.

EXPERIMENTAL.

3 : 4-*Dimethoxyphenylethylamine*.—This amine has been prepared by Mannich and Jacobson (*Ber.*, 1910, **43**, 189) Rosenmund Mannich and Jacobson [D. R. P. 247906, (1912)], whose methods were found to be not entirely satisfactory. The amine is best prepared by Hoffmann's reaction from 3 : 4-dimethoxyphenyl propionamide under the conditions described by Buck and Perkin (*J. Chem. Soc.*, 1924, **125**, 1679). The preparation of this amide has been described by Buck and Perkin (*loc. cit.*) who record the unsuitability of preparing it from the acid chloride. However, under the conditions specified below it can be used with success.

The 3 : 4-dimethoxycinnamic acid was prepared by heating veratric aldehyde (50 g.), malonic acid (65 g.), pyridine (100 c.c.) and piperidine (5 c.c.) on the steam-bath for an hour and then the reaction completed by boiling the solution for 5 minutes. The product was cooled, poured into water and acidified with hydrochloric acid and the nearly quantitative yield of dimethoxycinnamic acid collected. This was reduced by $2\frac{1}{4}\%$ sodium amalgam as prescribed by Perkin and Robinson (*J. Chem. Soc.*, 1907, **91**, 1080). The well-dried 3 : 4-dimethoxyhydrocinnamic acid (50 g.) was mixed with benzene (200 c.c.) and small portions of thionyl 'chloride (40 c.c.) added from time to time with shaking. The mixture is allowed to remain for 24 hours, moisture being excluded. The excess of thionyl chloride and benzene was then removed under greatly reduced pressure at 35° as far as possible. The residue is then dissolved in a little fresh benzene and poured cautiously to a well cooled solution containing sodium hydroxide (15 g.) and concentrated ammonia (600 c.c.). The benzene is removed by distillation and the amide crystallised from hot water, m.p. 121°—122°. The yield averages 28-30 g. The yield is better with smaller quantities. Meconine carboxylic acid and its chloride were prepared exactly as described by Perkin, Ray and Robinson (*loc. cit.*).

Preparation of the Amide (I).—The chloride prepared from meconine carboxylic acid (10 g.), in benzene (35 c.c.) was mixed with a solution of homoveratryl amine (10 g.) in benzene (40 c.c.) and pyridine (4 c.c.). The mixture was cooled and not allowed to become warm. After staying for 24 hours, the reaction was completed by warming on the steam-bath for 10 minutes. The product well

washed successively with water, sodium carbonate solution, and dilute hydrochloric acid is freed from benzene and crystallised twice from hot dilute alcohol, m.p. 185°. (Found: N, 3·67. $C_{21}H_{23}O_7N$ requires N, 3·5 per cent.).

Oxypalmatine.—Meconine carboxy-β-veratrylethylamide (I) (4 g.) and freshly distilled phosphoryl chloride (30 c.c.) were gently heated together on the steam-bath for 8 hours. The mixture after remaining for 12 hours was decomposed by crushed ice and water and the liquid filtered from small residue. The bright yellow filtrate was rendered faintly alkaline with sodium hydroxide solution under strong cooling. The ocherous faintly yellowish base was collected. This was not crystallised and was directly reduced with acetic acid (50 c.c.) and zinc dust (20 g. added in two equal portions) by boiling for 30 minutes. The filtered solution was concentrated on the water-bath and then diluted with water. This was repeatedly extracted with relatively large volume of ether. The dried ethereal solution was concentrated and the residue dissolved in a little of alcohol and treated with potassium hydroxide (1 g.) in water (5 c.c.) for 5 minutes at about 70°. Water (150 c.c.) was now introduced and the precipitate collected. This was thrice crystallised from boiling alcohol with the aid of charcoal. The substance crystallises in pale yellow wooly needles, m. p. 194°—196°.* (Found : C, 68·4; H, 5·9. $C_{21}H_{21}O_5N$ requires C, 68·6 ; H, 5·7 per cent.).

The substance exhibits a strong bluish-violet fluorescence in strong daylight. The solution of the substance in 50% sulphuric acid gives with a drop of nitric acid on dilution a bright purple colour. This is much deeper than the corresponding colour obtained with oxyberberine and is more stable. The substance gives a much stabler acetate than oxyberberine.

The insoluble residue obtained in the above experiment was crystallised from acetic acid and was found to contain chlorine. The substance was not obtained in sufficient quantity for detailed investigation. Therefore the similar compound obtained in the case of oxyberberine was prepared in larger quantity and investigated (*cf.* Perkin, Ray and Robinson, *loc. cit.*, p. 744). The substance

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* Haworth, Koepfli and Perkin describe it as buff coloured prisms, m. p. 188°. The substance found in the present investigation was compared with oxyberberine and except that the two substances had different m. p.s no other difference in properties physical and chemical could be detected.

(III) crystallised in yellow rectangular prisms from acetic acid (thrice), then from benzene and finally from ethyl acetate, m. p. 229°—230°. (Found: C, 61·85; H, 4·1; N, 3·98. $C_{18}H_{14}O_5NCl$ requires C, 61·45; H, 3·8; N, 3·8 per cent.).*

The best thanks of the author are due to Prof. R. Robinson, F.R.S., for his kind interest and to the Chemical Society (London), for a grant which defrayed a part of the cost of the investigation. The author is also indebted to Prof. P. C. Mitter for the gift of pure opianic acid.

* These analyses were done by the micro-method by Fein Chemie, G. m. b. H. of Tübingen.

Photochemical Reaction between Bromine and (1) Cinnamic Acid, (2) Stilbene.

Part II.

By Rukminimohan Purkayastha and Jnanendra Chandra Ghosh.,

In a previous paper (this *Journal*, 1926, **2**, 261) the results of investigations on reaction between bromine and (1) cinnamic acid, and (2) stilbene in carbon tetrachloride solution were published. White light was used for illuminating the system. It was found that the velocity of reaction can be roughly expressed by a unimolecular equation with respect to bromine. A reference to Tables VIII to XIII in that paper will at once indicate that the unimolecular velocity constant increases a little during the first few minutes, attains a maximum and then diminishes as the concentration of the reacting constituents diminishes, the magnitude of the diminution being 10 to 12 per cent. It was considered necessary to decide definitely whether these variations were due to experimental error or whether they are determined by the mechanism of the reaction.

It was also shown in that paper that the rate of reaction depended upon the concentration of the acceptor molecules of stilbene or cinnamic acid, the inverse of the rate of reaction plotted against the inverse of the concentration of acceptor molecules giving a straight line. Berthoud (*Faraday Soc. Disc.* held in Oct., 1925, published in March, 1926) has given the following mechanism of the reaction,

$$Br_2 + h\nu \longrightarrow 2Br$$

$$A + Br \longrightarrow ABr$$

$$ABr + Br_2 \longrightarrow ABr_2 + Br$$

$$2ABr \longrightarrow 2A + Br_2 \quad \text{or} \quad 2ABr \longrightarrow ABr_2 + A$$
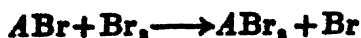
and obtains the following equation for the velocity of reaction.

For strong absorption $\frac{dx}{dt} = kI^{\frac{1}{2}} \left[Br_2 \right]$.

For weak absorption $\frac{dx}{dt} = kI^{\frac{1}{2}} \left[Br_2 \right]^{\frac{1}{2}}$

"The rate of reaction is obviously independent of the conc. of the acceptor as long as this concentration is not very weak." This statement is in contradiction to the result we have obtained before. The reaction was therefore subjected to a thorough re-investigation specially in view of the fact that Berthoud has not published his experimental data by means of which the accuracy of our results could be checked.

EXPERIMENTAL.

The methods of investigation were the same as before except that in the measurement of the incident radiation a Moll thermopile and a Moll galvanometer were used. By the aid of coloured filter solutions recommended by Plotnikow, parallel beams of blue and green light were isolated and their photochemical action was studied separately. The following filters were used :—

   (1) For blue light between $\lambda = 494\mu\mu$ to $458\mu\mu$
      (a) methyl green 0·2 gm. per litre (1 cm. thick).
      (b) copper sulphate 150 gms. per litre (2 cm. thick).
   (2) For green light between $\lambda = 540\mu\mu$ to $505\mu\mu$
      (a) potassium chromate 200 gms. per litre (2 cm. thick).
      (b) copper chloride 600 gms. per litre (2 cm. thick).

The reaction vessel used in the experimental had the following dimensions :—

Height	Breadth	Thickness
2·0 cm.	1·5 cm.	1·5 cm.

It was necessary for purposes of exact interpretation of experimental data that the molecular extinction coefficient of bromine for various wave-lengths in the solvents used should be known. This was measured by means of the König-Martens spectrophotometer. The values of molecular extinction coefficient are given in Table I.

TABLE I.

Solvent	Molecular extinction coefficient of bromine.					
	$592\mu\mu$	$579\mu\mu$	$546\mu\mu$	$533\mu\mu$	$488\cdot5\mu\mu$	$436\mu\mu$
CS_2	4·4	8·54	24·51	31·5	86·2	198·4
CCl_4	2·68	5·5	15·6	19·7	50·1	97·6

It will be noticed that throughout the visible spectrum the extinction coefficient of bromine in carbon disulphide is 1·5 to 2 times that in carbon tetrachloride solution. In the molecule of carbon tetrachloride all the valencies of the atoms constituting the molecule are more or less completely saturated and hence the field of force round the molecule is very weak. In carbon disulphide however, the field of force round the molecule is much larger due to the unsatisfied latent valencies of the sulphur atoms. The larger extinction coefficient of bromine in carbon disulphide may be due to a complex produced by the association of carbon disulphide molecule with bromine.

The Influence of Concentration of Acceptor Molecules on the Velocity of Photobromination.

For accurate determination of this factor the following simplifying conditions were adhered to.

(a) Blue light was used; the extinction coefficient of bromine for this light being very large, the whole of the incident radiation is practically absorbed even by dilute solution of bromine, there being no appreciable variation of absorbed radiation for small changes in concentration of bromine during the course of the reaction.

(b) The initial concentration of the acceptor molecules, as will be evident from Table II, was always in excess of the concentration of the photoactive bromine molecules.

(c) A definite but small period of induction has been noticed before; to avoid this initial disturbance two concentrations of bromine x_1 and x_2 were measured 6 and 20 minutes after starting the reaction. It will be at once evident from Table II that the concentration of cinnamic acid for each experiment during this

17

interval of 14 minutes did not change preceptibly as the change in the conc. of bromine during this time never exceeded ·002 M. If Berthoud's equation,

$$-\frac{2\cdot 8}{t}\ \log\ \frac{x_1}{x_2}=k\ \ \text{were correct,}$$

the values of k would have remained constant throughout. The values of k as obtained experimentally are recorded in colnmn 3 of Table II. They show a regular diminution as the initial concentration of cinnamic acid diminishes.

<div align="center">

TABLE II$_a$

</div>

Solvent-CS$_2$.   Temp. 30°C   Blue light.

Initial concentration of bromine in each experiment$=0\cdot0071$ M

Conc. of cinnamic acid.	Osmotic pressure in mm.	k	k^1
·06 M	1121·8	·0455	21·98
·03 M	560·9	·0425	23·53
·0225 M	420·6	·0391	25·57
·015 M	280·6	·0356	28·1
·01 M	187·0	·029	34·48

The inverse of osmotic pressure plotted against the inverse of k gives a straight line. Extending the equation of Turner (see our previous paper, *loc. cit.*, p. 261) to this case we obtained for

$$A a' \tau = \frac{\text{Intercept}}{\text{Slope}} = \frac{18\cdot9}{30\cdot3} = 0\cdot00623.$$

from which $\tau=2\cdot24\times10^{-10}$ sec., where τ is the life period of the excited photosensitive constituent.

Table III gives the experimentally determined values of τ for photobromination under different conditions of experiment.

TABLE III.

Solvent.	Acceptor.	$Aa^2\tau$
CS_2	Cinnamic acid	0·00628
CS_2	Stilbene	0·0185
CCl_4	Cinnamic acid	0·0021
CCl_4	Stilbene	0·0063

It is accordingly necessary to modify the equation and also the reaction mechanism by Berthoud in a way which will make possible a systematic explanation of our experimental results. It should be pointed out at the outset that in our previous paper we obtained the equation (loc.cit., p. 267),

$$\frac{dx}{dt} = C(a-x)\frac{\tau}{T+\tau}$$

where $(a-x)$ is the concentration of molecular bromine, τ is the life-period of the excited photosensitive constituent and T the interval between collision of the excited component and the acceptor molecule. The method of deduction of this equation as given before appears now to have been unsound in that the extinction coefficient of bromine was considered to be small. This statement is true for white light as a whole, but the velocity of reaction has been now found to be mostly determined by the blue and green radiations in the wave train, and the extinction coefficient of bromine for these radiations is very large (see Table I).

Our experimental results which are recorded in this paper in Table IV to XIV can be best explained by the following mechanism of reaction:

$$Br_2 + h\nu \longrightarrow 2Br \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$
$$Br + Br_2 \longrightarrow Br_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$
$$Br_3 \longrightarrow Br + Br_2 \quad \ldots \quad \ldots \quad \ldots \quad (3)$$
$$Br_3 + A \longrightarrow ABr_2 + Br \quad \ldots \quad \ldots \quad \ldots \quad (4)$$
$$2Br \longrightarrow Br_2 \quad \ldots \quad \ldots \quad \ldots \quad (5)$$
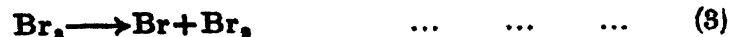
A chain mechanism leading to the regeneration of bromine atom necessary in order to account for our experimental observation

that under different experimental conditions the number of dibromide molecules formed varies between 50 and 150 (Table ' XIX) for each quantum of light absorbed. The fourth process determines the speed of the reaction: (3) and (4) render back the bromine atoms consumed by (2). Thus (1) and (5) are in continual equilibrium and the concentration of free bromine atom at any instant is given by the relation,

$$k_1 I [1 - e^{-\epsilon[Br_s]l}] = k_s [Br]^\bullet$$

$$\text{or} \quad [Br_s] = \sqrt{\frac{k_1}{k_s} I. \ [1 - e^{-\epsilon[Br_s]l}]}$$

for green and blue light ϵ is very large;

$$\therefore \quad [Br] = \sqrt{\frac{k_1}{k_s}} I.$$

Assuming that all molecular species involved in this reaction except Br_s is pretty stable, but that Br_s has a very short life-period τ, it follows that the concentration of Br_s at any instant is practically determined by reactions (2) and (3) and has the value

$$[Br_s] = \frac{k_s}{k_s} [Br] \ [Br_s]$$

This is only true if the life-period of Br is not too small to allow of the application of the law of mass action in its ordinary form to (2). The rate of formation of the dibromide and hence the rate of disappearance of bromine is (from 4) proportional to the concentration of Br_s at any instant multiplied by the factor $\tau/T+\tau$ where T is the interval between the collision of a Br_s molecule and an acceptor molecule of stilbene or cinnamic acid.

$$\frac{dc}{dt} = k_4 \ [Br_s] \ \frac{\tau}{T+\tau}$$

$$= \frac{k_s}{k_s} \sqrt{\frac{k_1}{k_s}} I. \ [Br_s] \ \frac{\tau}{T+\tau}$$

$$= k \sqrt{I}.(a+x) \ \frac{\tau}{T+\tau}$$

But $\tau = Aa^\bullet p$ where p is the osmotic pressure in mm. of the acceptor molecules. Again $p = k\theta (c-x)$ where $(c-x)$ is the concentration of acceptor in gm. mols. per litre, θ the absolute temperature and k is a constant which can be easily evaluated (Van't Haff's Law).

Hence $\dfrac{dx}{dt}=k\ \sqrt{I.}\,(a-x).\dfrac{\tau A a^{2}k\theta\,(c-x)}{1+\tau A a^{2}k\theta\,(c-x)}$

putting $\tau A a^{2}k\theta=B$,

$$\frac{dx}{dt}=k\sqrt{I.}(a-x).\frac{B\,(c-x)}{1+B(c-x)}$$

or $dx\left[\dfrac{1+B\,(c-x)}{B\,(a-x)\,(c-x)}\right]=k\sqrt{I}\,dt.$

or on integration

$$\frac{1}{t}\ \log\frac{a}{a-x}+\frac{1}{t\ B(c-a)}\ \log\frac{a(c-x)}{c(a-x)}=k\sqrt{I}=k_{1}.$$

In Table IV-XVI the values of k_{1} given in column 3 are calculated from the above equation. The values of k_{2} given in column 4 are obtained from the simple unimolecular equation.

It will be seen that the velocity of reaction at the initial stage shows a progressive increase for a period varying between 5 to 15 minutes. This is due to the fact that during this stage the concentration of Br as determined by the equation (1) and (5) is on the increase. To avoid this initial disturbance the velocity constants given in the tables are calculated from the second reading as the initial value.

TABLE IV.

Green light; Intensity= ·15 Hefner ;

Solvent CS_{2}; Acceptor—cinnamic acid ; Initial conc.—·0238 M
Temperature 30°C; $B=120$.

Time in min.	$(a-x)$—conc. Br_2 mols. per litre.	k_1	k_2
0	·0197	...	...
8	·01756	...	...
16	·01455	·0324	·0235
25	·012	·0314	·0224
35·5	·009	·0318	·022
53·5	·00675	·0308	·0205

TABLE V.

Intensity=1 Hefner.

Time in min.	$(a-x)$—conc. Br$_2$ mols.per litre.	k_1	k_2
0	·02628	...	...
5	·02085	...	...
9·5	·0149	·105	·0742
15	·0099	·110	·0741
20·2	·0073	·108	·0690
31	·0045	·0099	·0588

TABLE VI.

Solvent CCl$_4$; Intensity=1 Hefner; $B=40$.

	·01962	...	...
17·5	·01532	...	...
39·5	·01117	·0307	·0143
84	·00675	·0291	·0123

TABLE VII.

Intensity=0·15 Hefner.

Solvent CS$_2$; Acceptor—stilbene; Initial conc.—0·0238 M

Temp. 30°C ; $B=360$.

0	·0197	...	...
15	·0185	...	...
33·7	·0158	·0121	·0107
54·5	·0123	.0121	·0105
75	·01085	·0114	·0098

TABLE VIII.

Intensity=1 Hefner.

Time in min.	$(a-x)$—conc. Br_2 mols. per litre.	k_1	k_2
0	·02628	...	...
16	·0156	...	...
27	·01037	·0473	·037
36	·00775	·0470	·035

TABLE IX.

Blue light; Intensity=1 Hefner.

Solvent CS_2; Acceptor—Cinnamic acid; Initial Conc.—0·0258 M. Temp. 30°C; $B=120$.

0	·0197	...	...
11	·01575	...	...
20	·0111	·058	·039
27	·00855	·059	·038
33·5	·00675	·060	·0377
41·5	·00525	·059	·036

TABLE X.

Blue light; Intensity=·066 Hefner

Solvent CS_2; Acceptor—cinnamic acid; Initial conc.—0·0238M. Temp. 30°C ; $B=120$.

0	·02628	...	...
8·5	·01362	...	...
11	·0103	·208	·158
14·1	·00782	·206	·090

TABLE XI.

Solvent CCl_4 ; Intensity $= \cdot 1$ Hefner ; Temp. 30°C ; $B = 40$.

Time in min.	$(a-x)$—conc. of Br_2 mols. per litre.	k_1	k_2
0	·01962	...	...
12	·0183	...	...
35	·0145	·0223	·01
55	·01215	·022¦	·00955
108	·0075	·0239	·00928

TABLE XII.

Acceptor—stilbene.   Intensity $= 0\cdot66$ Hefner; $B = 120$.

0	·02617	...	...
20	·02197	...	...
31	·0183	·0244	·0166
41	·0156	·0247	·0163
52	·0132	·0254	·0159

TABLE XIII.

Solvent CS_2 ; $B = 360$.

0	·02628	...	...
10	·0201	...	...
16·1	·0135	·078	·065
28	·0092	·077	·061

TABLE XIV.

Time in min.	$(a-x)$—conc. of Br_2 mols. per litre.	k_1	k_2
0	·0197	...	...
5·8	·01522	...	...
9	·0128	·074	·067
14	·00905	·074	·0635

TABLE XV.

Blue light.

Solvent	Intensity	Acceptor	k_1	k_2
CCl_4	·66	Cinnamic acid	·075	·026-·024
CCl_4	·66	Stilbene	·0246	·017-·016

A comparison of the columns 3 and 4 in the tables given above will show that while k_2 undergoes regular diminution in value with increase in time, the values of k_1 are more or less conconcordant. This uniformity in the value of k_1 is evidence in favour of the mechanism of reaction we have proposed. It should be pointed out that while in green light the constancy of the values of k_1 is always much better than that of k_2, in blue light however, in some of our experiments, k_1 has a tendency to increase slightly as the reaction progresses. There is one drawback however in that other experimental conditions remaining the same, the ratio of the velocity constants k_1 is not proportional to the sq. root of the ratio of the incident intensities. In Table XVI, the ratio of velocity constants are compared with intensity ratios.

TABLE XVI.

Quality of light.	Solvent.	Acceptor.	$\dfrac{k_2}{k'_2}$	$\dfrac{k_1}{k'_1}$	$\dfrac{I}{I'}$	$\sqrt{\dfrac{I}{I'}}$
Blue	CCl_4	Cinnamic acid.	$\dfrac{·025}{·0096}=2·6$	$\dfrac{·075}{·0227}=3·3$	6·6	2·57
Blue	CS_2	,,	$\dfrac{·1}{·0377}=2·65$	$\dfrac{·21}{·059}=3·5$	6·6	2·57
Green	,,	,,	$\dfrac{·069}{·022}=3·14$	$\dfrac{·11}{·032}=3·44$	,,	,,
Green	,,	Stilbene	$\dfrac{·086}{·0105}=3·4$	$\dfrac{·047}{·012}=3·9$	,,	,,

18

It will be noticed that for blue light the ratio of the simple unimolecular constants k_s is approximately equal to the square root of the incident intensities ; for green light this is not the case. The ratio of the velocity constants is much larger than $\sqrt{I'I'}$ but always much less than $I'I'$. It is possible that simultaneously with the formation of bromine atoms, excited molecules of bromine may be produced by the absorption of light and these may cause a chain mechanism of the following type.

$$Br_2 \rightleftharpoons Br_2 \text{ (excited)}$$
$$Br_2 \text{ (excited)} + Br_2 \longrightarrow Br_2 . \ Br_2 \text{ (excited)}$$
$$Br_2 . \ Br_2 \text{ (excited)} + A \longrightarrow ABr_2 + Br_2 \text{(excited)}.$$
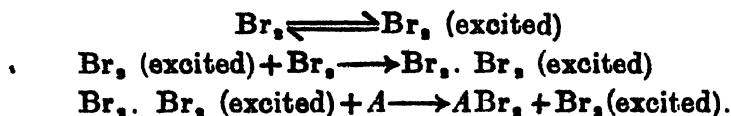
It is obvious that for strong absorption of light according to this mechanism of reaction,

$$kI = k_1^\bullet = \frac{1}{t} \log \frac{a}{a-x} + \frac{1}{t \ B \ (c-a)} \ \log \frac{a(c-x)}{c(a-x)}$$

k_1 will be proportional to the incident intensity. If these two processes happen simultaneously the ratio of velocity constants will lie between the simple ratio of the intensities and the sq. root of their ratio.

It may be argued that the diminution of the value of k_s is not due to diminution in the concentration of the acceptor molecules but is due to the fact that the whole of the incident blue or green radiation is not absorbed by the bromine solution and for that reason the amount of light absorbed diminishes as the concentration of bromine decreases during the progress of the reaction. It is possible to calculate approximately the correction that should be applied to the unimolecular constant k_s if only this factor is to be taken into consideration. The original unimolecular equation has the form,

$$-\frac{dx}{dt} = kx \ \sqrt{I\left(1 - e^{-\epsilon.x.l}\right)}$$

or

$$x \ \sqrt{e^{-\epsilon.x.l}} = -k\sqrt{I} \ dt$$

or

$$\frac{dx}{x}\left[1 + \tfrac{1}{2} e^{-\epsilon.x.l} + \tfrac{1}{2}.\tfrac{3}{4}.e^{-2\epsilon.x.l} + \dots\right] = -k \ \sqrt{I} \ dt$$

or

$$\int^x \frac{dx}{x}\left[1 + \tfrac{1}{2}e^{-\epsilon.x.l} + \tfrac{1}{2}.\tfrac{3}{4}. \ e^{-2\epsilon.x.l} + \dots\right] = -k \ \sqrt{I} \ t$$

$$\text{or } \int_x^a \frac{dx}{x} + \tfrac{1}{2} \int_x^a \frac{e}{x}^{-\epsilon.x.l} \cdot d\epsilon + \tfrac{1}{2}\cdot\tfrac{2}{4} \int_x^a \frac{e}{x}^{-2\,\epsilon.x.l} \cdot d\iota + \dots$$
$$= k\sqrt{I}\,t$$

$$\text{or } \log\frac{a}{a-x} + \tfrac{1}{2}\left[\ lie^{-\epsilon.l(a-x)} - lie^{-\epsilon.l.a}\ \right]$$

$$+ \tfrac{1}{2}\cdot\tfrac{2}{4}\left[\ lie^{-2\,\epsilon.l(a-x)} - lie^{-2\,\epsilon.l.a.}\ \right] + \dots = k\sqrt{I}\,t$$

$$\text{or } \log\frac{a}{a-x} + S = k\sqrt{I}\,t$$

The values of $lie^{-\epsilon.l.a}$ can be obtained from De Morgan's "Calculus" and the values of S can be evaluated. This has been actually done and it was found that for blue light of $\lambda = 488\ \mu\mu$, the correction term S is always negligible. In the case of green light ($\lambda = 533\mu\mu$) in CCl_4 solution the value of S varies from ·0012 to ·0018 as bromine concentration varies from ·02 to ·01 M. In CS_2 solution the variation in the value of S is still smaller. It is clear therefore that this correction term is not at all sufficient to account for the regular diminution in the value of unimolecular constant k_s with the progress of reaction.

The temperature coefficient of the reaction between bromine and cinnamic acid has been determined in different regions of the spectrum. The experimental results are given in Table XVII.

TABLE XVII.

Temperature coefficient between 30° and 40°.

Solvent	Blue 488$\mu\mu$	Green 533$\mu\mu$	White-light
CCl_4	2·45	2·65	2·74
CS_2	2·7	2·8	2·85

It is evident from the result that the temperature coefficient increases with the wave-length of light. The dark reaction has no doubt a large temperature coefficient but the dark reaction is very small in comparison with the light reaction.

The relation between photochemical efficiency and wave-length of light is given in Table XVIII. It will be seen that in CCl_4 solution the number of molecules of cinnamic acid transformed into dibromide per quantum of light absorbed varies from 22 to 48, and in CS_2 solution the number is 3 to 4 times greater.

TABLE XVIII.

Temp.	Solvent	Acceptor	No. of mols. transformed per quantum of	
			Blue (488$\mu\mu$)	Green (533$\mu\mu$)
80°C	CCl$_4$	Cinnamic acid	43	22
,,	,,	Stilbene	34	16
,,	CS$_2$	Cinnamic acid	156	101
..	CS$_2$	Stilbene	99	52

Summary.

1. The photobromination of cinnamic acid and stilbene has been studied in CCl$_4$ and CS$_2$ solutions in blue and green light.

2. It has been found that there is a regular diminution in the value of the unimolecular velocity constant with increase in time. This has been explained by assuming the following mechanism for the reactions :—

$$Br_2 + h\nu \longrightarrow 2Br$$
$$Br + Br_2 \longrightarrow Br_3$$
$$Br_3 \longrightarrow Br + Br_2$$
$$Br_3 + A \longrightarrow ABr_2 + Br$$
$$2Br \longrightarrow Br_2.$$
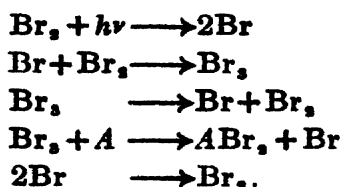
3. The temperature coefficient of the light reaction has been found to increase with the wave-length of incident radiation.

4. The average life-period of the intermediate activated molecule in the photobromination of cinnamic acid and stilbene has been determined and found to be of the order of 10^{-9} secs.

5. Molecular extinction coefficient of bromine in carbon disulphide for different wave-lengths has been measured.

6. In blue light the unimolecular velocity constant varies as the sq. root of the intensity of incident radiation but the increase is greater in green light.

7. The rate of reaction depends upon the concentration of the acceptor molecules.

8. The photochemical efficiency of the wave-lengths 488$\mu\mu$ and 533$\mu\mu$ for the bromination of cinnamic acid and stilbene has been measured. In the case of cinnamic acid in carbon tetrachloride the number of molecules transformed into dibromide per quantum of 488$\mu\mu$ is 43, of 533$\mu\mu$ 22. In carbon disulphide the number of molecules transformed per quantum is much greater.

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The Dependence of the Ionisation Potential of Elements on their Electronic Structure.

By R. N. Ghosh.

Our knowledge of the electronic structure of atoms which is successively due to Rydberg, Bohr, Main-Smith and Stoner, has been recently put in a diagramatic form by Saha and Ray (*Phys. Zeit.*, 1927, **28**, 221). The difference between the Saha scheme and Stoner's is as follows : Stoner has divided the L-level in three L_{11}, L_{21}, L_{22}, the M-level in five sub-groups, etc. Saha and Ray have shown that the division of each of the L_2, M_2, N_2 into two sub-groups is more apparent than real, the two sub-levels L_{21}, L_{22} ought to be united under one single L_2-level instead of being split up. Stoner's scheme has sometimes given rise to certain misconceptions. Some investigators assume that when the M_3-level is filled up, as for example in the transitional groups, either of the M_{32} or M_{33} sub-level is first filled up to its maximum number of electrons and then the other level begins to be filled up. Saha and Ray have shown that this conception is opposed to the actual structure of the outer shells as revealed by analysis of optical spectra, to account for which we have to assume that the electrons are not divided into two statically distinct sub-levels, but only in one M_2, or M_3 level. The optical terms are given by the synthesis of the quantum mechanical characteristics of these electrons, according to principles discovered by Russel, Pauli and Heisenberg and worked in full details by Hund (*Zeit. Physik*, **33**, 345; **34**, 296).

'This view is also supported from an examination of the progressive values of the ionisation potential of elements. It can be shown that the ionisation potential of a particular element rises gradually with the number of electrons in the outermost shell. When the

outer shell is completed the ionisation potential reaches a maximum value. The same thing may be said of the radiation potential. Thus when we consider the ionisation potentials of elements from boron to neon, or from aluminum to argon, in which in each case the L_2-level is being filled up, we find that the curve is uniformly rising and reaching a maximum value in neon and in argon respectively. The same may be said about the transitional group of elements in which the M_2 or the N_2 level is being gradually filled up, with one or two electrons in the N_1 or the O_1 level (see Fig. 2). Here also the curve shows a gradual increase reaching a maximum value when the shell is completed, after which there is a sudden drop when the next shell begins to be filled up. The curve as we take from scandium to nickel shows no maximum at any intermediate point as would be expected if there were a state of separation of electrons in two sub-levels M_2 and M_3 and, if the M_3-level was filled up after the M_2-level had received its complete quota of electrons namely four.

We have to explain how these values have been obtained. In some cases, e.g., in H and He, the value of I. P. is known from experimental data. But the results obtained from the electron bombardment method have always to be confirmed by results obtained from spectral classification of the lines of element. In order to be able to grasp the spectral data, I start with the general structure diagram of elements as given by Saha. (The diagram has been taken from the paper of Saha communicated to the Phys. Zeit., " Uber Eine Neue Karte des Aufbaus der Atome ").

To get the spectral terms, write out the full number of electrons under each level, for example taking Si we have to write 2 under K_1, 2 under L_1, 6 under L_2, 2 under M_1, then we are left with 2 under M_2. The constitution of the outer shell is now $2M_2$. To get the optical terms, we have to keep one electron running through the higher levels, and calculate the terms according to the rules given by Pauli, Heisenberg, and worked out by Hund. In this way, let us take all the elements successively.

H, He and Li.—The ionisation potentials are so well known that no discussion is necessary.

Beryllium.—In beryllium the terms expected will be apparent from the structure diagram.

CHEM. SOC. JOURNAL

R. N. GHOSH.

IONISATION POTENTIAL

Transition   Group III.

K
2

71 Lu	89 Ac
72 Hf	90
73 Ta	9f Br
74 W	92 Ur
75 Re	
76 Os	
77 Ir	
78 Pt	

1 H
2 He
3 Li ...... L₁
4 Be 2L₁
5 B .... L₂
6 C 2L₂
7 N 3L₂
8 O 4L₂
9 Fl 5L₂
10 Ne 6L₂

11 Na ...... M₁
12 Mg 2M₁
13 Al .... M₂
14 Si 2M₂
15 P 3M₂
16 S 4M₂
17 Cl 5M₂
18 A 6M₂

29 Cu ...10M₂ N₁ 9M₂
30 Zn 2N₁
31 Ga ...... N₂
32 Ge 2N₂
33 As 3N₂
34 Se 4N₂
35 Br 5N₂
36 Kr 6N₂

47 Ag ...10N₂ O₁
48 Cd 2O₁
49 In ...... O₂
50 Sn 2O₂
51 Sb 3O₂
52 Te 4O₂
53 I 5O₂
54 Xe ... 6O₂

70 Au ..... P₁
80 Hg 2P₁
81 Tl ...... P₂
82 Pb 2P₂
83 Bi 3P₂
84 Po 4P₂
85 Rad H ... 5P₂
86 Nt 6P₂

O_4
14

P_3
10

Q_2
6

The cha[ ]cessive X-ray levels. The subscript
' 1 ' denotes that [su]bscript ' 2 ' as in L_2, M_2 ..... denotes
that the electrons [ ]2 for X_1, 6 for X_2, 10 for X_3 etc......
r nd is obtained fr[ ]

Constitution.	Terms expected.	Terms found.
$2L_1$	$^1S_0$	75074 (?)
L_1L_2	$^1P_1$ ^3P	$^3P_1 = 53212$ $^1P_1 = 32431$ (?)
L_1M_2	$^1D_1$ ^3D	$^3D = 13137$

Though the triplet series have been obtained by Bowen and Millikan (*Physical Review*, **28**, 256) and the triplet terms ^3P and ^3S are known, no intercombinations have yet been determined. The above value of the ionisation potential has been obtained on certain assumptions. The ionisation potential cannot be very much different from the value given here, because the strong arc line λ 2348·7 is the line ^1S—$^1P_1$, and ^1P comes out to be 32431, *i.e.*, ca N/2'.

Boron.—The ionisation potential of boron (Bowen and Millikan, *Physical Review*, 1927, **29**, 232; also *loc. cit.*) has been calculated from the recent data of Bowen who finds the deepest term $^2P_1$ equal to 67546 and the corresponding ionisation potential comes out to be 8·4 volts.

Carbon.—The spectrum of carbon is one of the least known. According to the structure diagram the terms expected are as follows :— .

Carbon.

Combination.	Terms expected.	Terms found.
$2L_2$ ...	$^3P_{0,1,2}$, $^1D_2$, $^1S_0$	No value is accurately known.
L_2M_1 ...	$^3\bar{P}_{0,1,2}$ $^1\bar{P}_1$	

$^3P_{0,1,2}$ have the highest values. Bowen and Millikan (*loc. cit.*) have recently obtained combinations which Bowen interprets as being due to the transition,

$$2 L_1 2 L_2 \longleftarrow 3 L_1 L_2$$

$$(L_2 \longleftarrow L_1).$$

If the assignment be correct, the fundamental ^3P-terms have the successive differences 16 and 27, so that the line λ 2478 which alone

is obtained with the aid of ordinary spectrographs in the spectrum of carbon, arises either from $^1D_2$ or $^1S_0$ state. Assuming that it arises from $^1D_2$ (which alone gives us strong combinations), we can provisionally put

$$\lambda\ 2478.\ 3 = {}^1D_2 - {}^1P_1$$

and assign to $^1P_1$ the value of $N/2^2$, we have $^1D_2 = 67799$, the fundamental $^3P = {}^1D_2 + 11000$ from analogy with the differences between $^3P - {}^1D_2$ terms of other tetravalent elements like Si, Ge, Pb. (See MacLennan, *Trans. Roy. Soc., Canada*, 1926, **20**, 362). The I. P. comes out to be 9·7.

The ionisation potential of neutral silicon has not yet been accurately determined, because the higher Rydberg terms have not been traced. According to Fowler (*Phil. Trans.*, **225**, 1) the ionisation potential is about 7·5 volts. This can be wrong only by a small amount. Recently MacLennan (*loc. cit.*) has obtained a better value, *viz.*, 7·99 volts.

Nitrogen and Phosphorus.

Both have 3 P-electrons in the outer level.

The series classification of elements with 3P electrons in the outer ring is yet incomplete. According to the structure diagram the fundamental term and the next terms will be as follows :—

Nitrogen.

Combination.		Terms expected.	Terms found.
a) 3 L₂	...	$^4S_3$, $^2\bar{P}$, ^2D	117353 (Hopfield)
b) 2 L₂ M₁	...	$^4P_{1,2,3}$ ^2D ^2S, ^2P	33879 $^2P = 45083$ (Kiess).

Kiess and Kiess (*J. Optical Soc., America*, 1925, **11**, 1) have effected some classification in which the final orbit corresponds to (*b*). Hopfield (*Physical Review*, 1926, **27**, 801) recently announces that he has obtained a ^2D—term and he calculates from certain rather vague

analogies that $^4S_2 = 14\cdot48$ volts, but the value seems to be a bit too high. No connection seems to have been obtained between Kiess' and Hopfield's terms. The I. P. as given is subject to revision.

In the case of phosphorus, Sur (*Nature*, 1925, 542) has worked out the limiting value of a set of doublet term which can probably be identified with ^4P in the fundamental combination. If this view be correct then $^4S_2$ would have about a value of 72000 corresponding to the ionisation potential of 9 volts. This value is also uncertain.

Oxygen and Sulphur (six-valence electrons).

Values given by Hopfield (*Nature*, 1923, 437) have been adopted as they are apparently quite accurate.

Fluorine and Chlorine (five electrons in P-orbits).

According to the structure diagram the fundamental levels and the higher levels will be as follows.

Fluorine.

Combination.	Terms expected.	Values.
a) 5 L₂ ...	$^2P_{1,\,2}$	136900
b) 4 L₂ M₁ ...	$^4P,\ ^2P,\ ^2D,\ ^2S$	$^4\ddot{P}_2 = 46747$
		$^2\bar{P} = \ ?$
c) 4 L₂ M₂ ...	$^4\ddot{D},\ ^4P,\ ^4\ddot{S}$ $\Big\}$ $^2F\ ^2D\ ^2P$ $^2D,\ ^2P,\ ^2\ddot{S}$ $\Big\}$ ^2P	

Dingle (*Proc. Roy. Soc.*, 1926, **113**, 323) and De Bruin (*Zeit. Physik*, **39**, 869) have observed the quartet and doublet terms corresponding to the combinations (*b*) and (*c*). The value assigned by Dingle to *b* $^2\bar{P}$ is rather arbitrary. Bowen (*Physical Review*, 1927, **29**, 231) has recently announced terms corresponding to first combination. The value of the $^2\bar{P}$ terms has been found to be 136900 corresponding to an ionisation potential of 16·9 volts. As regards chlorine Turner (*Physical Review*, 1926, **27**, 397) has obtained lines arising from the fundamental ^2P level ; assigning to the *b* $^2\bar{P}$ term the approximate value of 3·2 volts which is intermediate between the values of corresponding terms of argon and sulphur, we obtain for its ionisation potential a value of 13·2 volts.

INERT GASES.
Neon and Argon.

Combination.	Terms.	Neon.	Argon.
(X=L, M) 6X$_1$	$^1S_0$	173910	127103
5X$_2$ Y$_1$	^3P ^1P	39110, 39470, 39887 38040	32557, 33361, 33967 31711
5X$_2$ Y$_2$	^3D ^3P ^3S	20958—25671	18388—23009
	^1D ^1P ^1S	11493—12419	11742—15285
5X$_2$ Y$_3$	^3F ^3D ^3P	about N/3^2	about N/3^2
	^1F ^1D ^1P		

In both these cases, series classification is complete. The fundamental orbit in the case of all the inert gases is $^1S_0$ and the next terms are ^3P and $^1P_1$. The line $^1S_0 - ^1P_1$ and $^1S_0 - ^3P$ have been obtained by Hertz and Lyman (*Zeit. Physik*, 1926, **31**, 469). The combinations and the expected terms are shown in the above table. In the case of neon and argon, ^1P and ^3P values are obtained from those given by Paschen (*Ann. Physik*, **60**, 405; **63**, 201) and Meissner (*Zeit. Physik*, 1926, **39**, 172) respectively, who have been able to trace Rydberg sequences. The values given are therefore strictly accurate.

TRANSITIONAL GROUP 1.
Sc to Ni.

The ionisation potential of these elements have been calculated from the following considerations :—

In none of the transitional group, the ionisition potential is yet accurately known, excepting in chromium (MacLennan, National Academy of Sciences, 1926, **12**, 726), manganese, (*Ann. Phys. Chem.*, Madrid, 1926, **21**, 42; see also M.A. Catalan, *Phil. Trans.*, 1922, **223**, 127) and molybdenum (*Bull. Bureau of Standards*, Vol. 19, p. 113). The constitution of the outer shell as given in the structure diagram has been obtained from analysis of the optical spectra, which is so far confined to the identification of the fundamental and the next set of terms. Sur has discussed how the Rydberg sequence even in such complicated spectra can be traced, but the task proposed is so laborious that it would take a long time before the full Rydberg sequences are obtained. The values of the ionisation potential as given above have been obtained from various considera-

tions which can be regarded only as approximate, but the actual values cannot differ by more than ·1 or ·2 volt.

Titanium.—Russel quoted by Payne (*Proc. Nat. Acad. Sci.*, **12**, 725) announces recently that the I.P.=6·8 volts and not 5·8 as originally announced by Kiess and Kiess. Russell's value seems to be a bit higher than what it ought to be. Since the paper has not yet come out, it is not possible to settle the point.

Iron, Cobalt and Nickel.—In case of Fe, Laporte (*Zeit. Physik*, **26**, 18) gives the I.P.=8·15 volts. He has traced two ⁹F terms which he thinks form a Rydberg sequence. In Co Sur has worked out the Rydberg sequence of ⁹F terms and the value 8·52 volts seems to be fairly accurate (unpublished work). In Ni, the value has been given by Kichlu, Bechert and Sommer (*Ann. Physik*, **77**, 351, 536) from the terms which are supposed to form Rydberg sequence. This value may not be quite accurate.

Atomic Number.	Element.	Ionisation Potential	Remarks.
1	H	13·54	
2	He	24·47	
3	Li	5·37	
4	Be	9·2	Calculated.
5	B	8·4	
6	C	9·7	Calculated.
7	N	14·5	Too high.
8	O	13·56	
9	F	16·9	
10	Ne	21·6	
11	Na	5·13	
12	Mg	7·61	
13	Al	5·96	
14	Si	7·9	
15	P	9·0	Approximate.
16	S	10·3	
17	Cl	13·2	
18	A	15·5	

Atomic Number.	Element.	Ionisation Potential	Remarks.
19	K	4·3	
20	Ca	6·1	
21	Sc	5·4	
22	Ti	6·8	Too high.
23	V	6·5	
24	Cr	6·7	
25	Mn	7·4	
26	Fe	8·2	
27	Co	8·5	
28	Ni	9·0	
29	Cu	7·7	
30	Zn	9·3	
31	Ga	5·97	

Summary and Conclusion.

A preliminary survey has been made of the elements of lower atomic number than Ga (31), but the data are not sufficiently accurate. The spectral classification also has not yet been completed. But from this preliminary survey, the main points raised in this paper have been confirmed, viz., there is a short period of 2 (corresponding to the formation of alkalis, and filling up of X-levels; a period of 6 (corresponding to the formation of the regular group of elements, ending in each case in an inert gas); corresponding to the filling up of X-levels; a period of 10 (corresponding to the formation of the transitional groups I, II, and III and filling up of the X-levels). The ionisation potentials of the Group constituting the rare earths are not known, because their spectral lines have not yet been classified.

In no case above treated, the existence of a subsidiary maximum, corresponding to the filling up of an M_2, M_3, or N_2, N_3 sub-level has been traced. It therefore, appears that Stoner's sub-levels are more apparent than real.

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Catalytic Formation of Methane from Carbon Monoxide and Hydrogen, Part III. A Study of Various Catalysts.

BY KSHITINDRAMOHAN CHAKRABARTY AND
JNANENDRA CHANDRA GHOSH

In a previous paper (*J. Indian Chem. Soc.*, 1925, **2**, 157) an attempt was made to prepare a catalyst which would transform blue water gas, in which hydrogen and carbon monoxide are present in almost equimolecular quantities, to a fuel gas where the percentage of carbon monoxide will be smaller than 20 and that of methane will be larger than 30. A reference to Table IV in that paper will show that at 406°, with nickel-pumice-sugar, carbon-vanadic oxide catalyst, the effluent gases satisfy this condition. The space velocity is rather low being only 5·7 c.c. of gas per minute per c.c. of catalyst space. In this paper will be described an account of a series of experiments carried out with the object of preparing a cata- lyst which will possess very much higher efficiency and will be at the same time steady.

In these investigations the quantity of catalyst taken in the re- action tube was very much smaller (only 6 g.) than in previous cases so as to make the fall in the activity of the catalyst easily detect- able. The same apparatus as was described in the first part (*loc. cit.*, p. 150) was used during these experiments. Reference to Table IV in Part II of these series will show that when the temper- ature of reaction was near 400°, the percentage of carbon dioxide present in the resulting gases, when an anhydrous mixture of carbon monoxide and hydrogen in the ratio of 1:1 was passed over the catalyst, was almost the same as that of methane. In the experiments recorded in this paper, only carbon dioxide in the resulting gases was estimated, and the percentage of methane formed was consider- ed to be approximately the same as that of carbon dioxide.

EXPERIMENTAL.

In the catalysts described below asbestos fibre was the support- ing material common to all.

Catalyst I.—*Nickel Hydroxide.*

A solution containing 1 gm. of nickel nitrate was added to 1 gm. of asbestos fibre so as to give a semi-solid mass. This mass was next treated with a dilute solution of sodium hydroxide, washed alkali free and dried. During washing nickel hydroxide not deposited directly on this fibre was mostly removed.

Catalyst II (A).—*Nickel Hydroxide and Manganese Hydroxide.*

A solution containing 1 gm. of nickel nitrate and 1 gm. of manganese nitrate was added to 1 gm. of asbestos fibre and treated as in the previous case.

Catalyst II (B).—*Nickel Hydroxide on Manganese Hydroxide.*

In this case manganese hydroxide was first deposited on asbestos fibre in the usual way and next nickel hydroxide was deposited on the product.

Catalyst II (C).—*Manganese Dioxide on Nickel Hydroxide.*

In this case deposition of manganese hydroxide followed that of nickel hydroxide.

Catalyst III (A).—*Nickel Hydroxide and Magnesium Hydroxide.*
Catalyst III (B).—*Nickel Hydroxide on Magnesium Hydroxide.*
Catalyst III (C).—*Magnesium Hydroxide on Nickel Hydroxide.*
Catalyst IV (A).—*Nickel Hydroxide and Zinc Hydroxide.*
Catalyst IV (B).—*Nickel Hydroxide on Zinc Hydroxide.*
Catalyst V (A).—*Nickel Hydroxide and Lead Hydroxide.*

Catalyst VI.—*Ammonium Vanadate on Nickel Hydroxide.*

Nickel Hydroxide was deposited on 1 gm. of asbestos fibre in the usual way. To the product a solution of 0·1 gm. of ammonium vanadate was added and the product dried up.

Catalyst VII.—*Chromium Acetate on Nickel Hydroxide.*

A solution containing 0·6 gm. of chromium acetate was added. Procedure was same as in the previous case.

Catalyst VIII.—*Ammonium Molybdate on Nickel Hydroxide.*

A solution containing 0·6 gm. of ammonium molybdate was taken. Procedure was same as in the previous case.

Catalyst IX (A).—*Nickel Hydroxide and Aluminium Hydroxide.*
Catalyst IX (B).—*Nickel Hydroxide on Aluminium Hydroxide.*
Catalyst IX (C).—*Aluminium Hydroxide on Nickel Hydroxide.*
Catalyst IX (D).—*Nickel Nitrate on Aluminium Hydroxide.*

A solution containing ·6 gm. of nickel nitrate was added to asbestos fibre upon which aluminium hydroxide was deposited.

In Table I are recorded the results of experiments carried out with the catalysts described above. The temperature of the catalyst before the reacting gases were passed over it, corresponded with that of the furnace and was 300° approximately. On passing the gas mixture at a constant rate, the temperature of catalysts mass rises rapidly as the reaction on its surface is an exothermal one. The temperature of the catalyst soon attains a maximum which is always higher than that of the furnace. The rate at which the temperature rises is a rough measure of catalytic power and the time during which the catalyst retained its maximum temperature indicates the duration of steady activity. The observation was corroborated by analysis of the effluent gases. It was also noticed that the rate of rise of temperature of the catalyst for a constant velocity of the gaseous mixture varied generally in an inverse ratio with the steadiness of the catalyst. It is well known that "excessive activity of catalyst is associated with maximum alterability" and our observation in the present case agrees with that view.

TABLE I,

Catalyst.	Rate in c.cs. per min.	Temp. °C	% of CO_2.	Remarks.
I	58	322	2	On starting the gas mixtures at the rate of 58 c.c. per min. temp. of the catalyst rose from 300° to 322° and was not steady.
II (A)	62	370	37	On starting the gas mixture at the rate of 62-66 c.c. per min. temp. rose from 310° to 370°. Within half an hour it lost much of its activity.
II (B) ...	59	323·25	11·2	On starting the gas mixture at the rate of 59-62 c.c. per min. temp. of the catalyst rose from 306° to 328.° Within 15 mins. the temp. again fell to 310°.
II (C) ...	66	372-74 (approx.)	30	On starting the gas mixture at the rate 66 c.c. per min. temp. rose from 306° to 375° (approx.), remained steady for 3-5 mins. and was followed by a rapid fall.

Catalyst.	Rate in c.cs. per min.	Temp. °C	% of CO_2.	Remarks.
III (A) ...	67	332	6	On starting the gas mixture at the rate of 67 c.c. per min. temp. rose from 305° to 332° and was followed by a rapid fall.
III (B) ...	67	355	31·5	On starting the gas mixture at the rate of 67 c.c. per min. temp. rose from 305° to 355°; fell back to 340° in about half an hour.
III (C) ...	62	310	1·6	Temp. rose from 303° to 310° only; rate of passing gas being 62 c.c. per min.
IV (A) ...	...	...	...	No rise of temp. could be seen on passing the gas mixture.
IV (B) ...	...	...	...	No rise of temp. could be seen on passing the gas mixture.
V ...	...	...	...	No rise of temp. could be seen on passing the gas mixture.
V1 ...	...	...	...	No rise of temp. could be seen on passing the gas mixture.
VII ...	...	...	...	Slightly active.
VIII ...	...	...	...	On passing the gas mixture at the rate of 64 c.c. per min. temp. rose from 300° to 311° only.
IX (A) ...	57	345-48	36	On starting the gas mixture at the rate of 57 c.c. per min. temp. rose slowly from 300° to 352°. The activity remained steady for about an hour and 45 mins.
IX (B) ...	61	350-51	36	On starting the gas mixture at the rate of 60 c.c. per min. temp. rose slowly from 300° to 350°. The activity remained steady for about 6 hours.
IX (C) ...	62	350	33	On starting the gas mixture at the rate of 65-60 c.c. per min. temp. rose slowly from 305° to 355°. The activity remained steady for about 5 hours.
IX (D) ...	65	355-57	40	On starting the gas mixture at the rate of 63 c.c. per min. temp. rose a bit rapidly from 305° to 362°. Activity was steady for about an hour. On removal of the catalyst from the reaction tube some of the particles showed pyrophoric properties.

From the preceding table it is clear that though some of the catalysts were very active even at the moderately high initial temperature (800°), they were never indefinitely steady. The catalysts associated with aluminium hydroxide however seemed to be promising. The rate of fall of activity was rapid in all the cases. The inactivity of the catalyst in which ammonium vanadate was used seems to be anomalous on the face of the fact that in the previous paper it was seen that vanadium oxide in presence of sugar carbon promoted the reaction. Zinc oxide associated with rare earth has been found by several investigators to catalyse the synthesis of methanol from carbon monoxide and hydrogen. The reaction, $2 CO + 2H_2 = CH_4 + CO_2$ may be considered to be made up of the two reactions,

$$CO + 3H_2 = CH_4 + H_2O$$
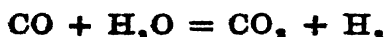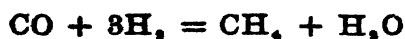
$$CO + H_2O = CO_2 + H_2$$

Medsforth (*J. Chem. Soc.*, 1923, **123**, 1452) suggested the following mechanism for the reaction: $CO + 3H_2 = CH_4 + H_2O$;

$CO + 2H_2 \longrightarrow H_2COH \longrightarrow :CH_2 + H_2O$; $:CH_2 + H_2 \longrightarrow CH_4$ Methanol being an intermediate product it was hoped that zinc oxide might help the reaction in question. It was not however realized.

An attempt was next made to see how far the activity of the pumice-sugar carbon-nickel catalyst could be increased by increasing the concentration of nickel in the catalyst and also to see whether the catalyst in that case would retain a steady activity.

Preparation of the Catalyst.

Always 10 g. of pumice stone (mixture of powder 2 small pieces) were taken with 2 g. of sugar. The volume of nickel nitrate solution added varied from catalyst to catalyst. Nickel nitrate solution used contained 0·0217 gm. of nickel per c.c. of the solution. Ammonium carbonate was used for preparing the fist two catalysts ; the procedure of preparation was practically the same as was described in part II of the series. After each day's work the catalyst was allowed to cool in a slow current of hydrogen. The quantity of catalyst taken inside the reaction tube was always 2 g.

TABLE II.

Catalyst prepared with varying quantities of nickel nirate solution.	Rate in c.c. per min.	Temp. °C	% of CO₂	Remarks.
I 20 c.c. sample ...	49	410	17·5	On passing the gas mixture at a rate of 49 c.c. per min. temp. of the catalyst rose slowly from 895° to 410°.
II 30 c.c. sample	56	427	38	On passing the gas mixture at the rate of 56 c.c. per min. temp. of the catalyst slowly rose from 390° to 430°.
III 50 c.c. sample	61	427	40	On passing the gas mixture at the rate of 61 c.c. per min. temp. of the catalyst rose slowly from 390° to 430°.
IV 60 c.c. sample	62	428	39	On passing the gas mixture at the rate of 62 c.c. per min. temp. of the catalyst rose slowly from 895° to 429°.
V 80 c c. sample ...	76	432	40	On passing the gas mixture at the rate of 75-80 c.c. per min. temp. of the catalyst rose from 895° to 440°.

It will be seen from Table II that the activity of the 30 c.c. sample is much greater than the 20 c.c. one. In the case of catalysts with higher conce ntration of nickel, the rise of activity was not marked. The rate of loss of activity in these catalysts was slow enough to escape quick detection. But slight deposit of carbon could always be seen in the catalysts on removal from the reaction tube.

From the study of the pumice-sugar charcoal-nickel catalyst it is evident that the rate of fall of acivity is very slow as opposed to the behaviour of non-sugar-charcoal catalysts described in this paper. It should be noted however that our attempt to obtain a catalyst of very high and steady efficiency at 400° has not been completely successful. In a forthcoming paper will be described the result obtained by using a mixture of water vapour, carbon monoxide and hydrogen as reactants.

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Note on Some Derivatives of Diphenylmethane.

By Kottiazath Narayana Menon.

During the last few years much attention has been given to the problem of the position in space of the phenyl groups in diphenyl, and a survey of the position has recently been made in the *Annual Report of the Chemical Society* (1926, p. 119-125).

The author has made numerous experiments with the object of preparing the hydrocarbon (I) but the results have not been published owing to the appearance of an almost identical piece of work by Sircar and De (*J. Indian Chem. Soc.*, 1926, **3**, 245). In both cases negative results were obtained. In continuation, the investigation was extended to derivatives of diphenylmethane, which both Kaufler (*Annalen*, 1907, **351**, 151 ; *Ber.*, 1907, **40**, 3250) and Montague and Van Charante (*Rec. trav. Chim.*, 1912, **31**, 843) had suggested might possess a folded structure similar to the one proposed by Kaufler for diphenyl.

While, this work was in progress, it was shown by Butler and Adams (*J. Amer. Chem. Soc.*, 1925, 47, 2610) that the deductions of Montague and Van Charante were incorrect and this rendered it unlikely that it would be possible to join the rings in diphenylmethane by a second likage (III). It seemed advisable, however, to record the results. For this purpose the removal of hydrogen bromide from the bromo derivative of 4-methyldiphenylmethane (II) or the elimination of iodine from 4:4'-di-iododiphenylmethane (IV) seemed to offer the greatest prospect of success.

(I) (II) (III) (IV)
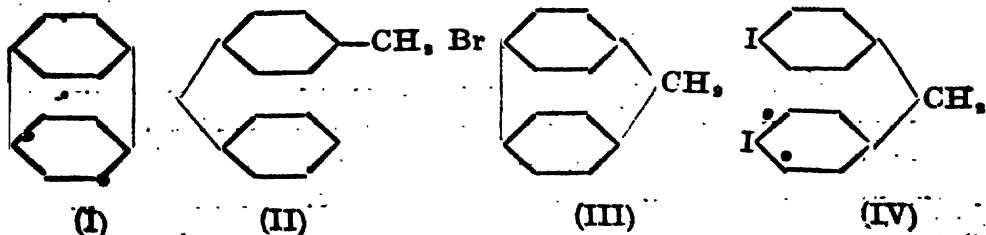
* The former of these two reactions was not investigated but a large number of experiments were carried out with the di-iodo deri-

vative. These experiments were uniformly unsuccessful and no evidence was obtained of the formation of the hydrocarbon.

Since it appeared possible that the halogen atoms might be more reactive in the presence of a nitro group, the nitration of 4:4'-dibromodiphenylmethane (V) was investigated.

Under the conditions described below the main product of the nitration was found to be 4:4'-*dibromo-*3:3'-*dinitrodiphenylmethane* (VI) the constitution of which was established by its oxidation to the corresponding benzophenone (VII) which has been described and orientated by Montague (*Ber.*, 1915, **48**, 1029).

$$Br\langle\rangle-CH_2-\langle\rangle Br$$

(V)

$$Br\langle\rangle-CH_2-\langle\rangle Br \quad (NO_2 \ldots NO_2)$$

(VI)

$$Br\langle\rangle-CO-\langle\rangle Br \quad (NO_2 \ldots NO_2)$$

(VII)
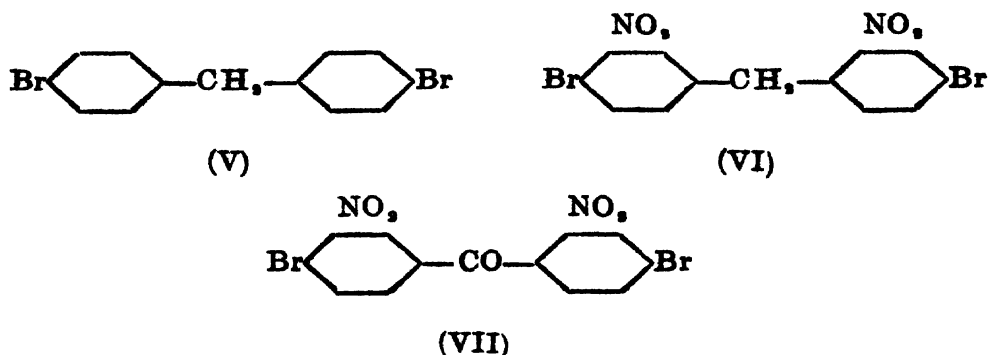
In this case also ring closure was unsuccessful.

EXPERIMENTAL.

4:4'-*Diododiphenylmethane.*—4:4'-Diaminodiphenylmethane (5 g.) was dissolved in dilute sulphuric acid (H_2O, 50 c.c.; H_2SO_4 10 g.) and diazotised in the usual manner with sodium nitrite. Potassium iodide solution (KI, 25 g.) was added to the cooled tetrazonium salt and the reaction mixture heated on the water-bath until all evolution of nitrogen had ceased. The solid which separated was collected and recrystallised from alcohol (yield 7·8 g.). 4:4'-*Di-iododiphenylmethane* crystallised in plates, m.p. 93-93·5° and was readily soluble in all the ordinary organic solvents. (Found: I, 60·4. $C_{13}H_{10}I_2$ requires I, 60·5 per cent.). As has already been mentioned attempts to eliminate iodine from this substance met with no success.

4:4'-*Dibromo-*3:3'-*dinitrodiphenylmethane.*—To 4:4'-dibromodiphenylmethane (2 g.) in acetic anhydride (5 c.c.) a mixture of nitric acid (d 1·42, 2 c.c.) and acetic anhydride (6 c.c.) was gradually added, the temperature being maintained at about 80°. When half the nitrating mixture had been added yellow crystals of the nitro compound

commenced to separate and the reaction mixture ultimately became a thick paste. After the addition of ice the solid was collected and recrystallised from amyl alcohol (yield 60 per cent.). The same product was obtained when the bromo derivative was added to fuming nitric acid at 0°.

4 : 4'-Dibromo-3 : 3'-dinitrodiphenylmethane crystalised from amyl alcohol in yellow needles, m.p. 238-240°. It was sparingly soluble in ordinary organic solvents. (Found: N, 7·0; Br, 38·4. $C_{13}H_8O_4N_2Br_2$ requires N, 6·7 ; Br, 38·5 per cent.).

4 : 4'-Dibromo-3 : 3'-dinitrobenzophenone.— 4 : 4'-Dibromo-3 : 3'-dinitrodiphenylmethane (2·5 g.) was dissolved in acetic acid and the hot solution gradually treated with chromic acid (2·5 g.) dissolved in acetic acid. When the oxidation was complete, water was added and the ketone collected. It was purified by crystallisation from benzene and melted, as stated by Montague (*loc. cit.*), at 157-158°. (Found: N, 6·8. Calc. N, 6·5 per cent.).

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Significance of Minimum Ionising Potentials of Gases in Relation to their Molecular Volumes.

By S. C. Biswas.

The displacement of an electron of any atom from its orbit in the stable condition is always associated with a certain amount of energy. Unless this amount exceeds a certain minimum value the atoms do not in general gain in energy. For the energy corresponding to $h\nu_r$ the atoms, however, just gain in energy and the electron is displaced from its most stable orbit to an unstable one, ν_r being the frequency of the first member of the absorption series, which is re-emitted in again falling back to the stable orbit. In this case, as can be seen, the electron is not driven to the extreme orbit of the atom or beyond the range of nuclear attraction. The energy corresponding to $h\nu_i$ where ν_i is the convergence frequency of the series for which ν_r is of the first member, gives the necessary energy for the atoms to be ionised and is known as ionisation potential, the term $h\nu_r$ being called resonance potential by Tate and Foote.

According to the electron theory, the electric doublet formed by the displacement of an electron relative to the central core, under the influence of an external electric field explains the polarisation of a medium. Considering the electron displacements in the case of the polarised media to be the same as in the cases of those by the absorption of minimum energy $h\nu_r$, Compton (*Phys. Review*, 1916, 8, 412) has shown that the natural frequency

$$\nu_r = \frac{1}{\pi} \sqrt{\frac{\pi N e^3}{m(K-1)}}$$

N being the number of molecules per unit volume, e and m the charge and mass of the electron, and K the dielectric constant.

If V_r is the minimum ionising potential,

then $$e.V_r = h\nu_r$$

or $$V_r = \frac{300h}{\pi e} \sqrt{\frac{\pi N e^2}{m \cdot K - 1)}}$$

Substituting the known values of constants e, m and h,

$$V_r = \frac{\cdot194}{\sqrt{K-1}} \cdot$$

The calculated values of V_r i.e., minimum or resonance poten-tials are in good agreement with experimental values. The value of K was derived from refractive index for infinite wave-length.

Di-electric Constant and the Molecular Volume.

On the modern belief of the structure of matter as presupposed in this calculation, the ring of electron or electrons in rapid orbital motion, constituting the outermost electron shell has been substituted for Mosotti's conducting sphere, and there is reason to believe that the radius of the displaced orbit under the influence of any external field must be greater than the calculated radius of Mosotti. That there is an appreciable field of force outside the outermost shell and it is due to this—that in an elastic collision between any two gas molecules, the separation is greater than the sum of their respective radii—has already been recognised by Jeans to explain the discrepency between Mosotti's values and those from gas laws (Jeans, "Mathematical Theory of Electricity and Magnet-ism," 3rd Edition, p. 188). It naturally strikes then, that the first resonance potentials which measure the work done in displacing an electron from the normal orbit to an orbit within the atom further removed from the nucleus must have some reference to the molecular volumes deduced from kinetic theory of gases. This expectation is realised to a certain extent in the Table I, column (IV) which shows that the product of molecular volume v and the

minimum potential V_r is a constant quantity within 5 to 6%. The molecular volume is calculated from the equation

$$v = \frac{b}{4} = \frac{1}{32} \times \frac{\theta_0}{273\pi_0} t$$

where b is the well known constant of equation of state, θ_0 and π_0 being critical temperatures and pressures.

TABLE I.

I	II	III	IV
Gases.	Molecular volumes.	Minimum ionising pot. (volts).	$V \times b$.
H_2	119	10·4[1], 10·2[11]	1296
He	105·0 } 99·5‡	19·7[2,3]	1950
Ne	76	16·84,[6] 16·6[3,5]	1261·6
A	144	8·22[66] 11·5 ± ·2‡‡ }	1186 } 1655
Kr	177	6·72[66] 9·7[6]‡‡ }	1189 } 1734·6
Xe	228	5·27[66] 8·3[3]‡‡ }	1204 } 1869·6
Ne	165‡ } 176	7·5[6,7], 7·4[11]	1287·5
CO	178	7·35,[10] 7·2,[6] 7·4[12]	1281·6
O_2	142	8·4,[6] 9·0[4,9]	1278·0
C_2H_6	252	5·1[10]	1290
F_2	130 (Cal.)	9·84[6]	1270
Cl_2	252 } 205	4·95[6] 8·2[11]‡‡ }	1247 } 1681
HCl	182 } 173	6·5[6] 9·3[11,9] }	1188 } 1608·9
H_2O	186 } 150	8·64,[6] 7·6[9]	1175

21

I Gases.	II Molecular volumes.	III Minimum ionising pot. (volts)	IV $V \times b$
NH$_3$	165	7·2	1188
CH$_4$	191 } 162‡ }	6·54* } 9·48[11]‡‡ }	1242 } 1526 }
NO	128	9·38[11]	1200·6
P$_2$ (vapour)	...	5·89[9]	...
S$_2$ (vapour)	264 (Cal.)	4·8[9]	1270
SO$_2$	247	5·35[6]	1259
CO$_2$	191	6·47,[6] 7·2[9]	1236
N$_2$O	198	6·26[10]	1219
CS$_2$	343‡	3·57[6]	1243

†   Molecular Volumes : Pease, *J. Amer. Chem. Soc.*, 1921, **43**, 991.

‡   Molecular Volumes of He, N, H$_2$O, CH$_4$, HCl, SO$_2$, CS$_2$; Kaye and Laby's *Tables.*

[1] "Origin of Spectra," Foote and Mohler, Edn. 1922 pp. 68, 74-77.

[2] Dejardin, *Ann. Physik*, 1924, 2 (X), 241.

[3] Hertz and Kloppers, *Zeit, Physik*, 1925, **31**, 463.

[4] Franek and Hertz, *Deut. Phys. Ges.*, 1913, (Jan. 30), p. 34.

[5] Horton and Davis, *Phil. Mag.*, 1921, **41**, 921.

[6] Compton, *loc. cit.*, p. 415,

[7] Brandt, *Zeit Physik*, 1921, **8**, 32 ; "Origin of Spectra," p. 190.

[8] Lockrow, *Astrophys. J.*, 1926, **63**, 205.

[9] Franck-Jordan, "Quantum Sprungen," p. 286.

[10] Calculated by Compton's formula using K from Kaye and Laby's *Tables*, p. 84.

[11] Hughes and Dixon, *Phys. Review*, 1917, **10**, 495.

*   These values for minimum ionising potentials as calculated by Compton (*loc. cit.*) appear to be too low. It may be noted that these values may be obtained as exact differences between first excipation potentials recorded by Dejardin and Hertz and the third inflection points noted by Dejardin for these respective gases at $19 \pm ·5$; $15·5 \pm ·2$; $13 \pm ·5$ (*loc. cit.*).

N. B.   Excepting for He these values seem to be one and a half times greater than the corresponding values calculated by Compton. Thus the products $V \times b$ (col. IV) as noted against these values are also found greater.

Analysis of Molecular Volumes with regard to the Structure of Atoms.

The foregoing results can be shown to be quite in accordance with the structure of elements and compounds as suggested by Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543). Elements and compounds having the same number and arrangements of electrons in the outer layer but differing only in the magnitude and distribution of nuclear charges have been called by Langmuir as 'Iso-Steres.' In this sense and also in similarity of physical properties N_2 and CO, N_2O and CO_2 are found iso-steric on analysis of their minimum ionising potentials.

NO having eleven sheath electrons, Langmuir suggests that the structure is the same as that given for nitrogen molecule, the extra electron being imprisoned in the "octet comprising the shell." N_2, O_2, F_2 have got similar structures—that of a double neon and therefore their minimum ionising potentials also seem to be halves that of neon. Thus though the critical constants of F_2 are unknown, it seems probable to allot for it a co-volume term (b) very nearly 129. Pease (*loc. cit.*) has calculated the molecular volume of nuclear carbon atom of ethane, with which elementary Fl_2 is iso-steric, to be about 118. Similarly P_2, S_2, Cl_2 should have the same srtucture as of a double argon with half the minimum potential values of it. Value for P_2 seems to be very high. Co-volume term for sulphur is calculated to be 264 which seems to be justifiable on the basis of the known molecular volumes of Cl_2 and thus of double argon atom. The computed values of F_2 and sulphur can also be checked thus : on the knowledge of the structures of neon and argon or neon-like and argon-like elements it is expected that double the difference between the molecular volumes of F_2 and neon should equal to that of Cl_2 and A. Similarly double the difference in molecular volume of oxygen and neon should equal that of sulphur and argon.

Again, elementary sulphur and sulphur dioxide having the same number of disposable electrons seem to be iso-steric, and have approximately the same molecular volume and consequently the same structures. The arrangement of sheath electrons in the cases of SO_2 and S_2 seems to be the same as in the cases of CO and N_2 ; only with this difference that in the former cases there is one neon structure in excess, thus—

$$b_{CO} + b_{Ne} = b_{SO}$$

This coincidence lends support to the view of Pease (*loc. cit.*) that instead of CO and N_2 having condensed structure as Langmuir believed they may have a more general acetylenic structure *i.e.*, 2 octets sharing three pairs of electrons, as is common to these cases. It must not be forgotten however that sulphur dioxide is a polar molecule whereas sulphur is non-polar. Yet their contributions to change the molecular volume or minimum ionising potentials appear very small. Exactly in the same way carbon disulphide has the same number of sheath electrons as CO_2 and N_2O, and it may be reasonable to attribute the same outer structure to CS_2 and as CO_2 and N_2O have, with this modification that there should be two complete neon structures in the interior of carbon disulphide. Thus—

$$b_{CS_2} = 2b_{Ne} + b_{CO_2}$$

HCl, H_2O, NH_3, CH_4 have again the same number of disposable electrons whereas the number of atoms to act as nuclei are 2, 3, 4 and 5 respectively. Without distinguishing, in any very principal part, polar structures of HCl, H_2O and NH_3 from non-polar CH_4 it may be mentioned that sheath electrons are arranged in the same way or that

$$b_{H_2O} + b_{Ne} - b_{HCl} = b_{NH_3} - b_{H_2O} = b_{CH_4} - b_{NH_3}$$

is a constant, for one atom of hydrogen being in excess in each case.

Attempt to a Theoretical Interpretation.

On the assumption that electron is rigidly connected to central charge, the orbital energy of rotation of the electron becomes $\frac{1}{2} I \omega^2$ where I is the moment of inertia and ω the angular velocity of rotation of the electron (Richardson, "Electron Theory of Matter," Edn. 1916, p. 358). It is admitted that the energy necessary to remove an electron from an atom is equal to "its own kinetic energy" and that the energy corresponding to minimum ionising or resonance potential must necessarily be proportional to it. Thus then

$$I\omega^2 \propto h \nu_r$$
$$\propto e . V_r \text{ (Einstein's Law.)}$$
$$\text{or} \quad \omega^2 \propto \nu_r$$

The centrifugal force of the revolving electron which is proportional to x^2/R (where x is the linear velocity of the electron moving in an orbit of radius R) must be balanced by the electrostatic attraction between electron and the central charge in the stable orbit.

$$\text{or } x^2/R = \omega^2 R \propto \frac{1}{KR^2} \text{ or } \omega^2 \propto \frac{1}{KR^3} \text{ i.e. } v_r \propto \frac{1}{KR^3}$$

As for all gaseous media K is very nearly equal to unity,

v_r becomes proportional to $1/v$ or $V_r \propto 1/v$

Conclusion.

From the results of column (IV) it appears that $v \propto \sqrt{K-1}$ is in contrast to Landolt's equation stating $\sqrt{k-1/d}$ is constant, or to Lorentz, Mosotti equation $K-1/(K+2)d$ is constant. The present equation also shows that V_r/d is constant, which states therefore that the specific work required to displace an electron measured by the minimum ionising potentials or more properly the specific minimum ionising potentials for different gases may be calculated which should have the same significance as Lorentz equation.

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Adsorption of Acids by Cocoanut Charcoal and Acetylene Carbon.

By D. Namasivayam.

Experiments with Cocoanut Charcoal.

These experiments were performed during 1922-23, but owing to certain interruption it was not possible to put together the results immediately then.

There are not any results known to me with reference to the adsorption of acids by cocoanut charcoal covering the same field as the investigation communicated in this paper. Some of the experiments on adsorption by cocoanut charcoal were made using the charcoal prepared from the inside kernal and not from the outside shell. Firth (*J. Chem. Soc.*, 1921, **119**, 926) in his study of adsorption of ammonia by cocoanut charcoal used the cocoanut shell for preparing the adsorbent. Driver and Firth (*J. Chem. Soc.*, 1922, **121**, 2409) in their study of adsorption of saturated vapours by charcoal used cocoanut charcoal prepared from both the shell and the fruit. But these and other investigators, I have come across, did not deal with acids in solution. In my experiments I have used the charcoal prepared from the outside shell of cocoanut and dealt with organic and inorganic acids in aqueous solution.

The experiments here described were undertaken to study the behaviour of cocoanut charcoal prepared from the outside shell of cocoanuts. It was also the intention to see if any general relation existed between the chemical constitution or the physical constants of the acids and the degree of adsorbability by a given adsorbent. Since the completion of the experiments described below, I have come across a paper by Fromageot and Wurmser (*Compt. rend.*, 1924, **179**, 972) who have investigated the relation between the degree of adsorption and the ionisation constant as well as the number of carboxyl groups of an acid. Though they did not use cocoanut charcoal, I find it interesting to give below, in the course of the

discussion of my results, a summary of their observations and show how they compare with mine.

Preparation of Cocoanut Charcoal.—The cocoanut shells used were those of ordinary kind obtainable in Madras. After removal of rasp, the shells were broken into small pieces. The broken pieces were charred well-covered with sand in an iron tray over a ring-burner. It took 3 to 4 hours to char all the pieces thoroughly. Out of every 100 gms. of original shell pieces, 30 to 40 gms. of charred shell pieces were obtained. They were powdered coarsely at first and finely afterwards. The powder was sieved through a fine mesh (90 to 100 meshes per inch), dried for 12 hrs. in an air-oven at 150° and cooled in a desiccator before use. The density of the powder was found to be 1·45 gms. per c. c. The ash in the charcoal was found to be 1·18 per cent. The extraction of the charcoal with concentrated hydrochloric acid reduced the ash to 0·68 per cent.

Preliminary Experiments.—Experiments were undertaken to determine the effect of time of shaking on the rate of adsorption, and it was found that the amount of oxalic acid adsorbed by cocoanut charcoal increased with increased periods of continuous shaking at first rapidly and then slowly. It was further found that in practice letting the solution stand with the charcoal for 5 to 7 days with occasional shaking, say 3 or 4 times a day, gave satisfactory equilibrium concentration. In the following experiments the solution was allowed to stand in well-stoppered bottles for a week in contact with the charcoal with occasional shaking in room temperature (27°—30°).

Experimental Details. The purest specimens of acids available in the laboratory were used in each case. The solutions of required concentrations were prepared (five dilutions from about 0·20 molar to 0·05 molar) and put in stoppered bottles. In similar bottles weighed amounts (about 1 gm.) of charcoal were introduced, and then 50 c.c. of each of the solutions were added, and allowed to stand for a week with occasional shaking. The original solutions also were allowed to stand in the stoppered bottles for the same period. Afterwards both the original solution and the solution added to the charcoal were titrated carefully using standard dilute baryta solution. For titration measured quantities of the clear solution over the charcoal layer were taken with a graduated pipette.

Experimental Result. From the experimental results so obtained I calculated the values of the equilibrium molar concentration of

D. NAMASIVAYAM.
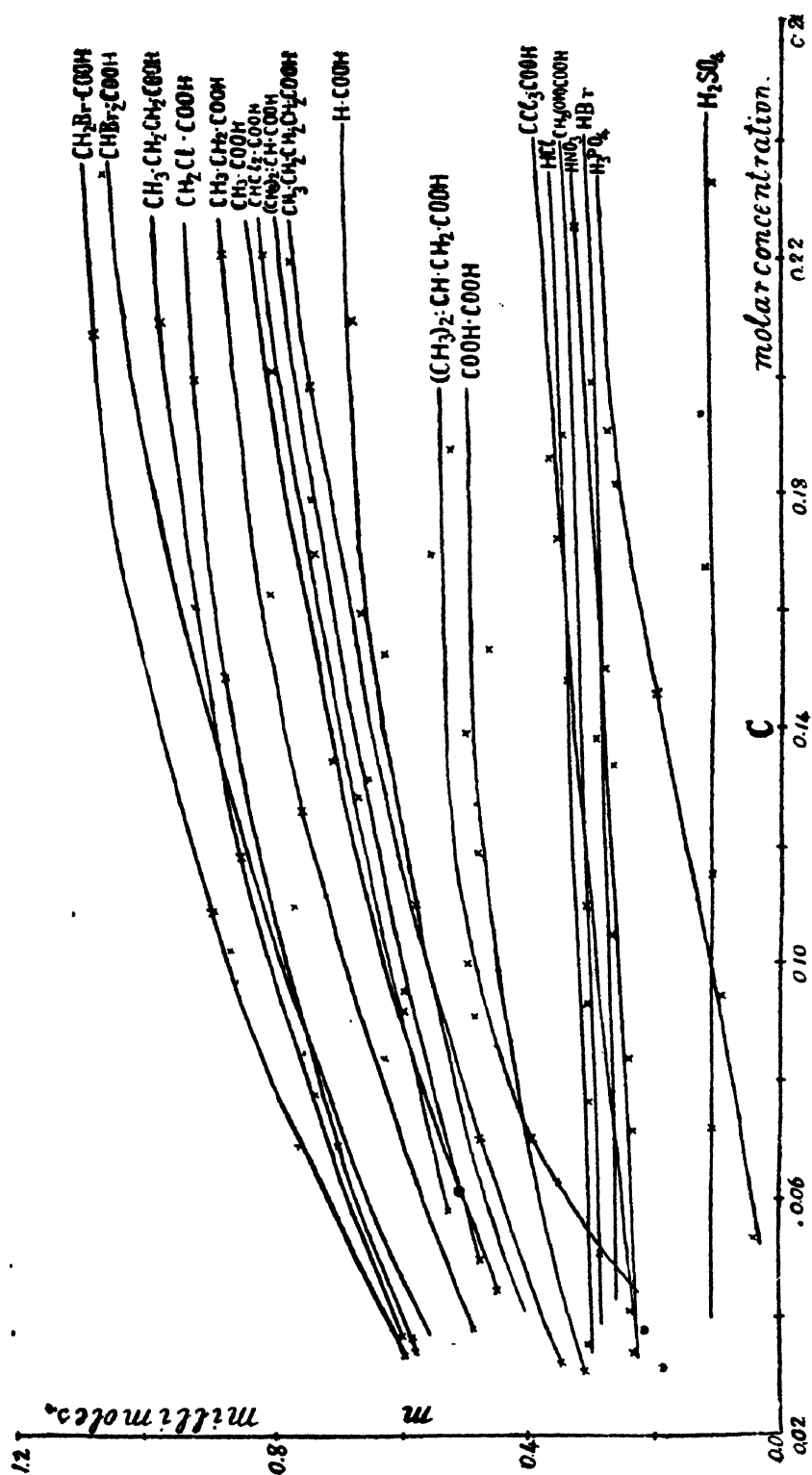
Fig. 1.
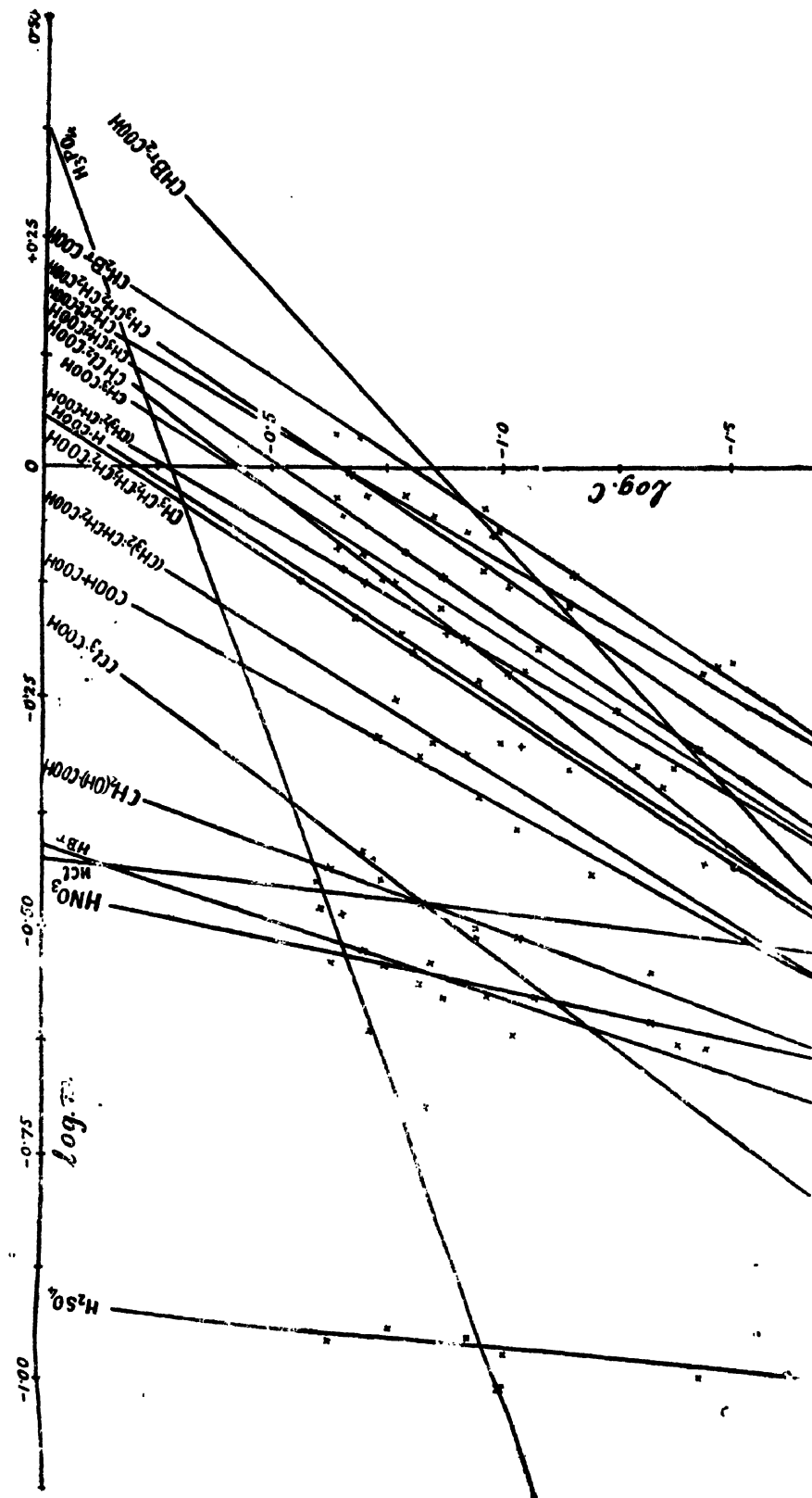
Fig. 2.

the solution after adsorption and of the number of millimoles of solute adsorbed per gram of charcoal.. The results were plotted and graphs drawn (Figs. 1 & 2). The graphs show that, within the dilutions studied, the adsorption of most of the acids examined follow the adsorption equation,

$$m = a \; C^{1/k} \quad ,$$

where m is the number of millimoles of solute adsorbed per gram of charcoal ;

    C is the equilibrium molar concentration of solution after adsorption ;

and a and k are constants.

I calculated the mean values of a and k for the cases examined. I have tabulated the values of C, m, a and k obtained (Table I).

<div align="center">

TABLE I.

Cocoanut Charcoal.

</div>

Serial No.	Name of acid.	Expt. No.	C	m	a	k
I. •	Formic acid	1	0·2727	0·758		
		2	0·2090	0·686		
		3	0·1592	0·674	1·16	2.88
		4	0.0913	0·489		
		5	0·0499	0·479		
II.	Acetic acid	1	0·2281	0·845		
		2	0·2000	0·805		
		3	0·1310	0·699	1·38	2.96
		4	0·1174	0·656		
		5	0·0575	0·526		
III.	Propionic acid	1	0·2196	0·886		
		2	0·1617	0·808		
		3	0·1261	0·760	1·48	2.94
		4	0·0689	0·628		
		5	0·0384	0·494		

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Serial No.	Name of acid.	Expt. No.	C	m	a	k
IV.	Butyric acid	1	0·2079	0·964		
		2	0·1608	0·931		
		3	0·1180	0·851	1·72	2.90
		4	0·0776	0·736		
		5	0·0370	0·603		
V.	Valeric acid	1	0·1976	0·753		
		2	0·1519	0·638		
		3	0·1099	0·576	1·15	2·81
		4	0·0702	0·483		
		5	0·0359	0·372		
VI.	Mono-chloracetic acid	1	0·1993	0·931		
		2	0·1477	0·881		
		3	0·1046	0·855	1·58	3·22
		4	0·0693	0·701		
		5	0·0336	0·584		
VII.	Dichloracetic acid	1	0·2204	0·819		
		2	0·1690	0·743		
		3	0·1277	0·665	1·51	2·54
		4	0·0920	0·603		
		5	0·0458	0·454		
VIII.	Trichloracetic acid	1	0·1897	0·366		
		2	0·1478	0·386		
		3	0·1101	0·306	0·68	2·77
		4	0·0719	0·242		
		5	0·0344	0·236		
IX.	Mono-brom-acetic acid	1	0·2060	1·077		
		2	0·1092	0·900		
		3	0·1016	0·868	1·85	3·00
		4	0·0692	0·761		
		5	0·0386	0·609		

Serial No.	Name of acid.	Expt. No.	C	m	a	k
X.	Dibrom-acetic acid	1	0·2908	1·800		
		2	0·2327	1·073		
		3	0·1834	1·115	2·82	2·05
		4	0·1101	0·769		
		5	0·0867	0·590		
XI.	Hydroxy-acetic acid	1	0·2362	0·364		
		2	0·1859	0·374		
		3	0·1383	0·289	0·47	5·14
		4	0·0933	0·311		
		5	0·0514	0·285		
XII.	Dimethyl-acetic acid	1	0·2189	0·774		
		2	0·1780	0·754		
		3	0·1313	0·655	1·19	3·42
		4	0·0948	0·600		
		5	0·0418	0·478		
XIII.	iso-Propyl-acetic acid	1	0·1694	0·556		
		2	0·1394	0·501		
		3	0·1191	0·478	1·07	2·83
		4	0·1003	0·496		
		5	0·0630	0·357		
XIV.	Oxalic acid	1	0·1869	0·506		
		2	0·1525	0·474		
		3	0·1192	0·440	0·79	3·70
		4	0·0703	0·399		
		5	0·0307	0·305		
XV.	Hydrochloric acid	1	0·2485	0·353		
		2	0·1717	0·364		
		3	0·1078	0·306	0·38	19·1
		4	0·0772	0·310		
		5	0·0328	0·311		

Serial No.	Name of acid.	Expt. No.	C	m		
XVI.	Hydrobromic acid	1	0·2564	0·328		
		2	0·1986	0·301		
		3	0·1495	0·278	0·39	7·12
		4	0·1049	0·270		
		5	0·0463	0·248		
XVII.	Nitric acid	1	0·2246	0·327		
		2	0·1809	0·268		
		3	0·1339	0·272	0·35	5·69
		4	0·0840	0·273		
		5	0·0407	0·238		
XVIII.	Sulphuric acid	1	0·2331	0·112		
		2	0·1667	0·115		
		3	0·1169	0·113	0·12	23·8
		4	0·0720	0·109		
		5	0·0351	0·101		
XIX.	Phosphoric acid	1	0·2389	0·291		
		2	0·1902	0·245		
		3	0·1462	0·202	2·40	0·71
		4	0·0937	0·089		
		5	0·0588	0·042		

Discussion of Results.—The results were examined to see if there is any well-marked relation between the chemical constitution or the physical constants of acids and their degree of adsorbility or the

values of a and k with reference to the adsorbent used, namely, cocoanut charcoal. The following points are worth noting in this connection. The adsorption isotherms of mineral acids approximate more towards straight lines than those of organic acids within the range of concentrations studied. The values of k for formic acid and its homologues are nearly equal. The value of k is greater generally for strong mineral acids than for weak organic acids (cf. hydrochloric with acetic acid). In the series from formic to butyric acid the values of a increase, while for valeric acid the value of a is smaller than that for butyric acid. Substitutions in the acids affect both a and k (cf. the substituted acetic acids), a being more susceptible than k. Repeated halogenation seems at first to enhance and then to diminish the values of both a and k of acetic acid. Chlorine, bromine and hydroxyl substitutions have different effects on the degree of adsorption of acetic acid. While the values of a for nitric, hydrochloric and hydrobromic acid are practically the same, the value of a for sulphuric acid is much less and that for phosphoric acid is much more. Phosphoric acid, though a weak acid, is not adsorbed to a greater extent than the strong mineral acids. The degree of adsorption of organic acids is generally greater than that of mineral acids. The adsorbability increases from formic to butyric acid but decreases from butyric to valeric acid. Increase in the number of carboxyl groups lowers the adsorption of the acid (cf. acetic and oxalic acid). There seems to be no general relation between the ionisation constants or the molecular structure of acids and the degree of adsorbability or the values of a and k of those acids.

From ageot and Wurmser (loc. cit.) have found that there is no simple relation between the degree of adsorption of different acids and their electrolytic dissociation constants. With this observation my results agree. They also found that the adsorbability increased with the number of carboxyl groups by comparison of acetic, succinic, oxalic and citric acid. My results regarding acetic and oxalic acid with cocoanut charcoal and with acetylene carbon show a contrary effect in the former case but a similar effect in the latter (see below). I have not used succinic and citric acid in my experiments. They have further found that salts have a smaller degree of adsorption than that of the corresponding acids. I have not dealt with salts at all in my investigations so as to be able to make such comparison.

Experiments with Acetylene Carbon.

Experimental Details.—When these experiments were being conducted, it was thought desirable to try some other adsorbent ; and acetylene carbon was tried at the suggestion of Prof. W. Erlam Smith. The acetylene carbon used was prepared by cooling a smoky acetylene flame (Fig. 3).
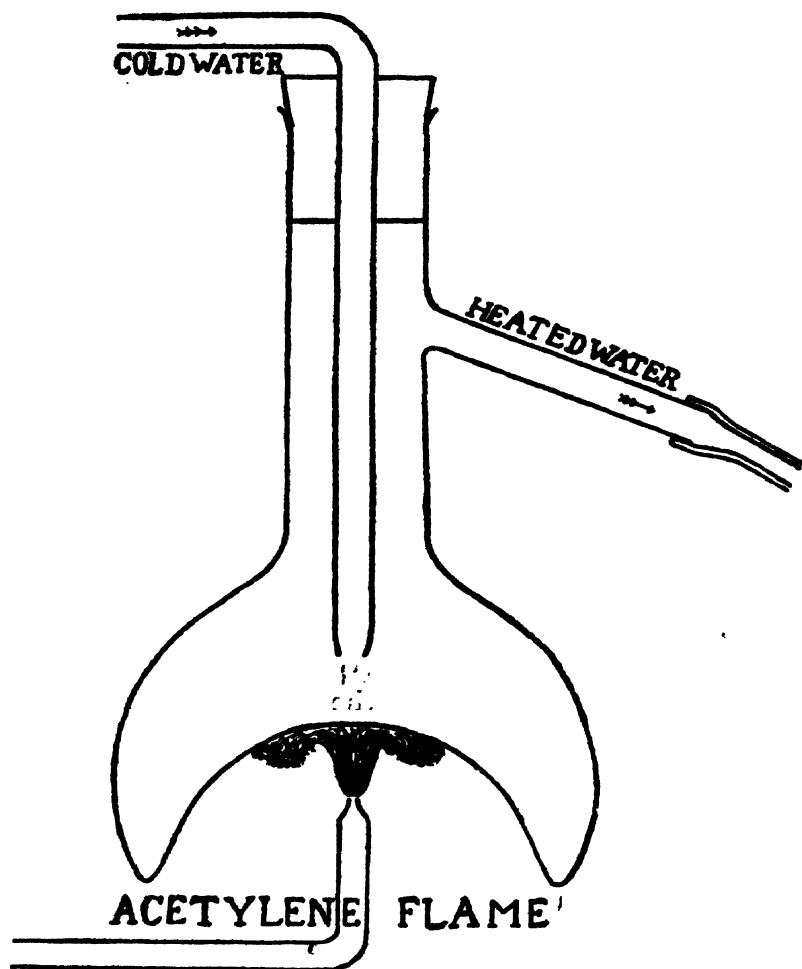
Fig. 3.

The carbon so obtained was collected, powdered and dried for 12 hrs. in an air-oven at 150°. It was found to contain 2·82 per cent. ash. The aqueous extract of the carbon was neutral to litmus. The adsorption of acetic and oxalic acid was tried with the help of this carbon and it was found that the concentrations of the solutions increased on being allowed to stand in contact with acetylene carbon (Table II).

TABLE II.

Acetylene Carbon.

Name of acid.	Expt. No.	C	m
Oxalic acid	1	0·480	—0·43
	2	0·217	—0·34
	3	0·107	—0·47
	4	0·026	—0·40
	5	0·023	—0·58
Acetic acid	1	1·260	—1·10
	2	0·292	—1·11
	3	0·262	—1·23
	4	0·226	—1·10
	5	0·181	—1·09
	6	0·126	—1·20
	7	0·111	—1·20
	8	0·096	—1·92
	9	0·085	—2·30

Discussion of Results.—It seems probable that more water was adsorbed by acetylene carbon than the acid adsorbed by it. The amount of the solute adsorbed is less, the more dilute the solution.

Pickless (*Chem. News*, 1920, **121**, 49) found in the case of wood charcoal and acetic acid solution that the ratio of

$C_{charcoal}$ (i.e., m) to C_{water} (i.e., C) varied from $+1·76$ to $+2·6$

depending upon the concentration of the solution. I find that (1) in the case of acetylene carbon and acetic acid solution, the ratio $m/C = -1$ to -25, and (2) in the case of cocoanut charcoal and acetic acid solution, the ratio $m/C = +4$ to $+10$. Pickles (*J. Chem. Soc.*, 1921, **119**, 1278) found that alkali halides were negatively adsorbed by wood charcoal.

Summary.

(1) Experiments were conducted in order to see if there is any simple relation between the degree of adsorption of acids and the chemical constitution or the physical constants of those acids. In these experiments cocoanut shell charcoal was used as the adsorbent.

(2) It was found that there was no direct relation between the degree of adsorption and the conductivity constants or the molecular structure of the acids examined.

(3) For the range of dilution studied (about 0·20 to 0·05 molar) the adsorption was in close agreement in most cases with the adsorption equation, $m = C^{1/k}$. For practical purposes m and C give respectively the concentrations of the solute in charcoal and in water in moles per kilogram. The adsorption isotherms of mineral acids approximate more towards straight lines than those of organic acids.

(4) It was found that the values of k for formic acid and its homologues were practically the same.

(5) The values of k were found to be greater for strong mineral acids than for weak organic and inorganic acids.

(6) The values of a were found first to increase and then to decrease in the series from formic to valeric acid.

(7) The values of a were found to be approximately the same for hydrochloric, hydrobromic and nitric acid.

(8) The nature and number of substitutions in an acid affect both a and k, a being affected to a greater extent than k.

(9) There seems to be no quantitative relation, however, between a or k and the ionisation constants or the molecular disposition of the acids.

(10) Increase in the number of carboxyl groups tends to lower the degree of adsorption in the case of cocoanut charcoal.

(11) Among the acids examined, sulphuric acid is least adsorbed. This may be so because of its great affinity for water.

(12) While the adsorption is positive in the case of cocoanut charcoal, the adsorption is negative in the case of acetylene carbon. That is, in the former case the solute is preferentially adsorbed, while in the latter case the solvent is preferentially adsorbed.

It seems desirable to pursue these experiments further especially with acetylene carbon, which would have been done already but for the unfortunate interruption referred to above. I hope to publish soon another paper on the adsorption of acetylene carbon.

Adsorption by Polar Precipitates. Part IV.
Further Experiments with Silver Salts.

By Jnanendra Nath Mukherjee, Jyoti Kanta Basu and
Asoke Mukherjee.

The present work was undertaken in order to obtain further data
on the adsorption of ions by insoluble polar precipitates with a view
to elucidate the nature of the process. It has been shown by
Mukherjee and Roy (this *Journal*, 1924, 1, 173), and by Mukherjee and
Kundu (this *Journal*, 1926, 3, 385), that though the order of adsorb-
ability of different ions by such precipitates on the whole runs
parallel to the order of increasing solubilities of the salts composed
of the ion in question and the oppositely charged ion in the precipi-
tate, there are striking exceptions. They also mention that in
general there is a strong adsorption of the constituent ions but here
also there are exceptions. The above authors base their conclusions
on electro-osmotic experiments which, they hold, give a better idea
of the relative adsorption of the ions of the electrolyte by the
surface. Analytical measurements, on the other hand, give the total
adsorption in the surface layer. Beekley and Taylor (*J. Phys.
Chem.*, 1925, 29, 943), from analytical measurements of adsorption
of silver salts by silver iodide, later came to the same conclusion as
that of Mukherjee and Roy regarding exceptions to the above
mentioned parallelism between solubility and adsorbability. The
conclusions drawn from variations in electrical charges of such
particles have a direct bearing on many analytical and related
problems in chemistry. Hahn, Erbacher and Feichtinger (*Ber.*,
1926, 59, 2014), in a very important paper, have recently shown the
existence of a relationship between the adsorption of a radio-
element by a polar precipitate and the electrical charge of the
surface. Their work fully confirms the contention of Mukherjee
(*Phil. Mag.*, 1928, 44, 321 ; *cf.* also Mukherjee and Roy, *loc. cit.*)
that the precipitation rule of Paneth (*Phys. Zeit.*, 1914, 15, 924) is
incomplete in so far as it does not take into consideration such types
of adsorption of ions as would lead to a change in the charge of

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the surface.   Hahn and co-workers critically examine the observations of previous workers and their recent measurements and show that the well-known generalisations of Fajans and Paneth regarding the carrying down of radio-elements by precipitates, which have been of so great a service to radio-chemistry, require to be modified and altered so as to include the following new generalisation :—

"Ein Element wird aus beliebig grosser Verdünnung an einem Niederschlage (Adsorbens) dann adsorbiert, wenn dem Niederschlage eine des ladung des zu adsorbierenden Elementes entgegengestiste Oberflächen—Ladung erteilt worden und die adsorbierte Verbindung in dem vorliegenden Lösungsmittel schwer löslich ist." Hahn points out that the above generalisation is in full agreement with the work of Mukherjee (*J. Indian Chem. Soc.*, 1925, 2, 191), and of Michaelis and Dokan (*Koll. Zeit.*, 1925, 37, 67).

In the present paper we have used three insoluble silver salts, namely, the chloride, bromide and iodide as adsorbent and solutions of silver and of sodium salts.   The experiments with silver salts enable us to compare our results with those from the analytical measurements of Taylor and Beekley.   Such a comparison has a good deal of theoretical interest and is likely to throw light on the nature of the adsorption of ions.

EXPERIMENTAL.

Three apparatus were set up for the three diaphragms.   The arrangement described in previous papers (*loc. cit.*) was used.   Every experiment was carried out under exactly similar conditions.

Preparation of the insoluble silver salts.

(i) *Silver Iodide.*—The procedure described by Beekley and Taylor (*loc. cit.*) has been rigidly followed.

(ii) *Silver Bromide.*—As with the iodide.   Washing was continued till the precipitate, on being kept in contact with conductivity water for a week, did not change the p_H to any appreciable extent.   The particles were fairly big in size and had well defined crystalline structure.   The salt, however, was not insensitive to light and so all the experiments were carried out in presence of light from a lamp with a ruby glass shield.

(iii) *Silver Chloride.*—Decinormal solutions of pure recrystallised potassium chloride and silver nitrate were prepared and mixed in darkness and allowed to settle for 48 hours. Fifty c. c. of a ten per cent. solution of ammonia were subsequently added to the colloidal mixture when the whole of the silver salt at once came down as heavy big particles ; washing was continued as above.

Three preparations of the iodide and two of the bromide did not show any change in the rate of movement of the bubble using conductivity water. This shows that these samples are reproducible so far as the rate of the movement is concerned (*cf.* Mukherjee and Kundu (*loc. cit.*) who found a difference).

Preparation of the Electrolytes.

(i) *Silver Nitrate.*—Merck's Reagent quality was recrystallised from conductivity water.

(ii) *Silver Nitrite.*—precipitated from pure recrytallised silver nitrate and sodium nitrite was washed free from the nitrate with water. It was next washed with absolute alcohol followed by ether. The latter was carefully evaporated and the sample was kept in an amber coloured vacuum desiccator. The whole operation was carried out in a dark room in presence of dim ruby lamp.

(iii) *Silver Acetate.*—precipitated from concentrated solutions of the respective recrystallised salts. The precipitate was redissolved in warm water, recrystallised and dried in an amber coloured vacuum desiccator.

(iv & v) *Silver Bromate and Benzoate.*—As above.

(vi-x) *Sodium salts* of arsenious, hydrobromic, sulphocyanic, acetic and salicylic acids were prepared by recrystallising Merck's 'reagent' samples.

Diaphragm.

The charge measurements were carried out at four different dilutions for each electrolyte, the concentration being N/1000, N/5000, N/10,000 and N/20,000. About 5 g. of the adsorbent material was washed several times with the solution in question and allowed to remain for 24 hours in a Jena glass stoppered bottle and transferred to the U-tube, and left undisturbed for 2 hours. The U-tube was dipped in a constant temperature bath. Four direct

and four reverse readings (for three minutes each) were taken. The mean of these are tabulated. The results are reproducible within 4 per cent.

The measurements of the charge in the case of bromide and chloride were carried out in a dark room with no light other than that of a photographic ruby lamp.

Results.

TABLE I.

Silver Iodide.

Conc.	AgNO₃	AgNO₂	Ag Acet.	AgBrO₂	Ag Benzoate.
N/0·0	—2·5	—2·5	—2·5	—2·5	—2·5
N/20,000	7·2	7·1	7·2	6·9	6·0
N/10,000	10·2	8·7	8·85	7·75	7·8
N/5,000	12·3	9·4	9·8	10·2	8·9
N/1,000	13·5	10·9	12·1	13·2	9·7

TABLE II.

Silver Bromide.

Conc.					
N/0·0	—3·1	—3·1	—3·1	—3·1	—3·1
N/20,000	8·0	7·6	8·5	7·4	7·5
N/10,000	10·1	8·2	8·4 (?)	8·0	8·0
N/5,000	12·5	10·1	10·6	10·75	10·0
N/1,000	14·7	11·0	14·65	14·0	10·1

TABLE III.

Silver Iodide.

Conc.	Na Arsenite.	NaBr.	NaSCN.	Na Acetate.	Na Salicylate.
N/0·0	—2·5	—2·5	—2·5	—2·5	—2·5
N/20 000	—4·2	—6·0	—12·3	—7·6	—8·0
N/10,000	—5·0	—6·5	—18·8	—9·1	—10·0
N/5,000	—7·2	—6·6	—20·0	—11·5	—12·3
N/1,000	—16·3	—7·2	—21·9	—15·0	—15·4

(?) 9·4 probably.

TABLE IV.

Silver Bromide.

Conc.	Na Arsenite	NaBr	NaSCN	Na Acetate	Na Salicylate
N/0·0	—3·1	—3·1	—3·1	—3·1	—3·1
N/20,000	—4·0	—4·2	—13·0	—4·2	—6·0
N/10,000	—7·3	—4·8	—19·2	—7·5	—8·3
N/5,000	—9·3	5·0	—21·4	—9·6	—11·0
N/1,000	—17·4	—9·7	—26·5	—16·8	—17·0

TABLE V.

Silver Chloride.

Conc.					
N/0·0		...	—4·3	—4·3	—4·3
N/20,000		...	—12·4	—5·1	—6·7
N/10,000		...	—18·25	—7·2	—8·3
N/5,000		...	—23·9	—9·45	—11·8
N/1,000		...	—27·3	—13·9	—15·2

For purposes of comparison we give below the solublities of silver salts.

TABLE VI.

Solubility of Silver Salts.

	Thiocyanate.	Bromide.	Arsenite.	Salicylate.
Solubility in millimols per g. H_2O	20°C 0·00000008*	20°C 0·0000004*	20°C 0·00003*	15°C 0·2089*

	Bromate.	Benzoate.	Nitrite.	Acetate.	Nitrate
Solubility in millimols per g. H_2O	20°C 0·006*	25°C 0·0114†	25°C 0·0259†	20°C 0·06*	20°C 4*

* Landolt and Bornstein's *Tables*.
*† Beekley and Taylor (*J. Phys. Chem.*, 1925, 29, 943).

Discussion.

Considering the adsorption of ions from the silver solutions we find in each case a rise in the positive charge, the originally negative charge of the precipitate becoming positive. The strong adsorption of silver ions observed previously is thus confirmed. As a result of the anion adsorption, the charges will be different. The adsorption of the anions is directly comparable as they are all univalent. The relative order of the adsorption of the anions remain the same throughout the range of concentration studied with the exception of the bromate and is the same for both the iodide and the bromide as adsorbents namely : benzoate > nitrite > acetate > nitrate. The bromate comes near the acetate at the higher concentrations though it shows greater relative adsorption at the lower concentrations. Its adsorption is throughout less than that of the benzoate ion. The order of increasing solubilities is bromate > benzoate > nitrite > acetate > nitrate. Excepting the bromate the two series are identical showing that the intensity of adsorption is related to solubility. Beekley and Taylor working with silver iodide as adsorbent find a different order of adsorbabilities : benzoate > acetate > nitrite > bromate > nitrate. It is possible that the analytical measurements of Beekley and Taylor do not give a correct idea of the relative adsorption of ions. In the present instance we are dealing mainly with a primary adsorption of silver ions and comparing equivalent concentrations of the different silver salts, the amounts of silver ions adsorbed per unit area of the same adsorbent should be identical if we assume that the anions are not primarily adsorbed. The anions from silver salts are possibly adsorbed in two ways : (a) primary adsorption on account of the affinity of the atoms on the surface ; (b) 'electrical' adsorption. The picture that we can form of the surface layer in contact with the solutions of the silver salts is that near each halide ion on the surface silver ions are primarily adsorbed, and near each silver ion anions are primarily adsorbed. In the case of such polar precipitates it is difficult to distinguish between primary and electrical adsorption excepting that in the case of primary adsorptions the ion is adsorbed in an unhydrated state and in the electrical adsorption a layer of solvent molecules probably intervenes between ions of opposite charge. Thus ultimate distribution of the different ions on the surface will be determined by the primary adsorption of the two ions as also by

the electrical adsorption of the two ions. In the present case we may neglect the 'electrical' adsorption of the silver ions because of the marked positive charge of the surface which shows that the 'fixed' layer on the surface always contains an excess of silver ions. The mobile sheet will contain an excess of the anions, and, if there be no exchange between anions in the solid and those in the liquid, from analytical measurements we ought to find an equivalent adsorption of both ions, mainly determined by the adsorption of the silver ions. The differences in the comparatively smaller amounts of adsorption of the anions will therefore be masked by the stronger adsorption of the silver ions, and if we consider the difficulties of correctly estimating small amounts of adsorption the discrepancy between the order of adsorption obtained by ourselves and that of Beekley and Taylor may be attributed in part to these factors. From their data we notice that the difference in the adsorption of nitrite and acetate at the higher concentration is such as to exclude this possibility. We have observed that the nitrite and the acetate have nearly the same adsorbability with the iodide as adsorbent and that the difference between their adsorption is greater when the bromide is the adsorbent. We would however mention that the adsorption experiments of Beekley and Taylor with acetate and nitrite were performed with two different samples of the precipitate possibly of different adsorbing capacities.

The stronger adsorption of the silver salts found by the above authors and by us is in agreement with the observation of Mukherjee and Kundu with silver iodide that the iodine ions are comparatively weakly adsorbed compared to that of the other constituent ion.

With the sodium salts we again observe that the order of adsorption of the anions is the same with the iodide, bromide and chloride as adsorbents. Arsenite behaves as the bromate does in the case of silver salts. The order of adsorption of these anions is thiocyanate > arsenite > salicylate > acetate > bromide. The order of increasing solubilities is thiocyanate > bromide > arsenite > salicylate > acetate. The comparatively weak adsorption of both the iodine and the bromine ions strengthens our conclusion regarding the weakness of adsorption of the constituent halide ions. The adsorptions of the nitrate ion and the chloride ion by silver iodide precipitates are comparable as appears from the work of Mukherjee and Kundu and that of Taylor and Beekley.

If we express the relative adsorption of the anions taking the data with silver acetate and sodium acetate as the basis of comparison we arrive at the following order of decreasing adsorption of anions:—

Thiocyanate> arsenite (?) > salicylate (?) > benzoate>nitrite> acetate> bromate (?) > nitrate> bromide (?), whereas the order of increasing solubilities is thiocyanate> bromide> arsenite> salicylate>bromate> benzoate> nitrite> acetate> nitrate.

Summary and Conclusion.

(1) The chloride, bromide and iodide of silver have negative charges in contact with water.

(2) The charge is reversed at a low dilution of silver salts.

(8) The order of adsorption of anions in silver salts by electro-osmotic method is benzoate> nitrite> acetate> nitrate.

Excepting the bromate this order is identical with the order of increasing solubility.

This order differs from the order of adsorption of these salts by silver iodide observed by Beekley and Taylor with respect to the position of acetate and bromate ions.

From experiment with sodium salts the following order of adsorption of anions is obtained: thiocyanate> arsenite> salicylate> acetate> bromide, which is the same as the order of increasing solubilities; the bromide forms an exception.

University College of Science
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Varying Valency of Platinum with respect to Mercaptanic Radicles. Part VI.

By Prafulla Chandra Rây, Kshitish Chandra Bose-Rây and Nadia Bihari Adhikari.

The action of bases on the complex compounds derived from chloroplatinic acid and thio-compounds (mercaptans, sulphides) has not only furnished valuable informations regarding the constitution of the complex compounds but has helped us in proving that the valency of platinum is variable (Rây, *J. Chem. Soc.*, 1919, **115**, 872; Rây, *ibid*, 1922, **121**, 1283; Rây, *ibid*, 1923, **123**, 133; Rây and Bose-Rây, *J. Indian Chem. Soc.*, 1925, **2**, 178; Rây, Guha and Bose-Rây, *J. Indian Chem. Soc.*, 1926, **3**, 155 ; Rây, Guha and Bose-Rây, *ibid*, 1926, **4**, 358).

The present work was undertaken with a view to throw further light on the interesting question of the variability of the valency of platinum. In this paper are described the results obtained by the action of ammonia and amine bases on the complex compound, $PtCl_2.(C_2H_4)_3S_3$ derived from chloroplatinic acid and triethylene trisulphide (Rây, *J. Chem. Soc.*, 1922, **121**, 1283).

The results indicate that most of the complex compounds can be represented on the Werner model, whereas others are to be regarded as molecular compounds. Indirectly the constitution of the complex compound appears to be

$$\left[\{(C_2H_4)_3S_3\} > Pt < {Cl \atop Cl} \right] Cl$$
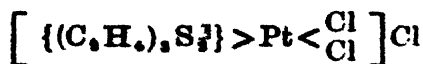
as will be evident from the following considerations :—

By the action of ammonia, $PtCl_2.(C_2H_4)_3S_3$ is converted into the well-known compound $PtCl_2.4NH_3$ (Carlgreen and Cleve, *Zeit. asorg. Chem.*, **1**, 67). This may be most conveniently represented on the Werner model as

$$\left[{NH_3 \atop NH_3} > Pt < {NH_3 \atop NH_3} \right] Cl_2$$
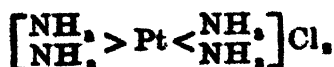
That the chlorine atoms in the above are ionisable has been proved by conductivity measurement (*vide* experimental). A

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compound of the same composition but not identical in physical properties has been obtained from ammonia and $PtCl_4$. $2 Et_2S$ by Rây, Guha and Bose-Rây, (this *Journal*, 1926, **3**, 156)

Benzylamine is found to give with $PtCl_2.(C_2H_5)_2S_2$ a compound having the composition $PtCl_2.4 C_6H_5CH_2NH_2$ which may be expressed by the Werner model, thus—

$$\left[\begin{array}{c}BzNH_2 \\ BzNH_2\end{array}>Pt<\begin{array}{c}NH_2Bz \\ NH_2Bz\end{array}\right]Cl_2 \quad \text{where } Bz=Ph.CH_2.$$

Any direct proof as to the ionisability or non-ionisability of chlorine cannot be adduced as no ionising solvent could be found. This compound has previously been obtained from $PtCl_2$. $2 Et_2S$ and benzylamine by Rây, Guha and Bose-Rây (*J. Indian Chem. Soc.*, 1926, **3**, 860).

By the action of ethylenediamine on $PtCl_2.(C_2H_5)_2S_2$, the following three compounds have been isolated :—

(i) $PtCl_2. 2C_2H_4(NH_2)_2$

(ii) $Pt_2Cl_6. 3 C_2H_4(NH_2)_2. (C_2H_4)_2S_3$

and (iii) $PtCl_2(C_2H_4)_2S_4$

Of these (i) is a well-known compound of the Werner type and may be represented in the following way (*cf.* Jorgensen, *J. pr. Chem.*, 1899, (2), **39**, 4, 1949).

$$\left[\begin{array}{c}CH_2\text{-}NH_2 \\ | \\ CH_2\text{-}NH_2\end{array}>Pt<\begin{array}{c}NH_2\text{-}CH_2 \\ | \\ NH_2\text{-}CH_2\end{array}\right]Cl_2$$
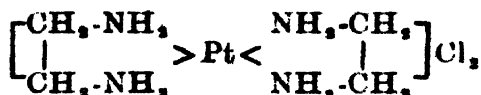
The ionisability of chlorine in the above has been shown by precipitation with silver nitrate.

The compound $Pt_2Cl_6.3C_2H_4(NH_2)_2.(C_2H_4)_2S_3$ is a molecular compound of $PtCl_2. 3 C_2H_4(NH_2)_2$ and $(C_2H_4)_2S_3$. Evidently the group (C_2H_4) is eliminated during the reaction giving rise to 1:4-dithian, which then polymerises to triethylene trisulphide (Rây and Bose-Rây, *J. Indian Chem. Soc.*, 1926, **3**, 73).

The compound $PtCl_4. (C_2H_4)_2S_4$ may be expressed either as a molecular compound of the type AgCl.NH or on the Werner type, thus :

$$\left[\{(C_2H_4)_2S_2\} >Pt<\begin{array}{c}Cl \\ Cl\end{array}\right]$$
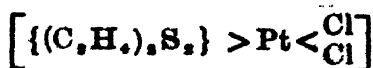
Pyridine acting on $PtCl_2.(C_2H_5)_2S_2$ produces three compounds, namely.

(i) Pt_2Cl_7, $4C_5H_5N$;

(ii) $PtCl_2$. $4C_5H_5N$;

and (iii) $PtCl_2$. $2C_5H_5N$.
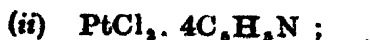
The compound (i) at the very first sight seems to be a molecular compound of $PtCl_4.2C_5H_5N$ and $PtCl_2. 2C_5H_5N$, but the substance could not be broken up into the component molecules owing to its insolubility in all common solvents.

Compound (ii) may be constituted as follows (*cf.* Kurnakow, *Zeit. anorg. Chem.*, **17**, 214)

$$\left[\begin{array}{c} Py \\ Py \end{array} > Pt < \begin{array}{c} Py \\ Py \end{array}\right]Cl_2 \quad \text{where Py=pyridine.}$$
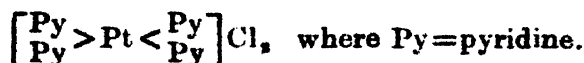
That the two chlorine atoms are ionisable has been proved by (i) the action of silver nitrate, and by (ii) conductivity measurements (*vide* experimental). The same compound has been obtained previously from $PtCl_2.2 Et_2S$ and pyridine by Rây, Guha and Bose-Rây (*loc. cit.*).

Compound (iii) may be represented on the Werner model thus (Jorgensen, *J. pr. Chem.*, 1886, [2], **33**, 504).

$$\left[\begin{array}{c} Py \\ Py \end{array} > Pt < \begin{array}{c} Cl \\ Cl \end{array}\right]$$
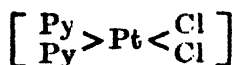
This compound is also obtained when $PtCl_2. 4C_5H_5N$ is heated to $140°$. During the change 2 molecules of pyridine are eliminated from the nucleus and 2 chlorine atoms enter the complex. The transformation may be shown thus :—

$$\left[\begin{array}{c} Py \\ Py \end{array} > Pt < \begin{array}{c} Py \\ Py \end{array}\right]Cl_2 \xrightarrow{-2Py} \left[\begin{array}{c} Py \\ Py \end{array} > Pt < \begin{array}{c} Cl \\ Cl \end{array}\right]$$
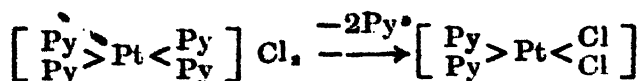
The same compound has been previously obtained by the interaction of pyridine and $PtCl_2.2Et_2S$ by Rây, Guha and Bose-Rây (*loc. cit.*).

Dimethylaniline is found to give $PtCl_2.C_6H_5N(CH_3)_2$ with $PtCl_2.(C_2H_5)_2S_2$. This compound cannot be expressed as a complex compound of the Werner type, but may be regarded as a

simple molecular compound of $PtCl_3$ and $C_5H_5N(CH_3)_2$ of the type of $AgCl.NH_3$.

By the action of piperidine on $PtCl_3.(C_2H_4)_3S_3$, $PtCl_3.$ $3C_5H_{11}N$ has been isolated. Probably it has the constitution :—

$$\left[\begin{matrix} C_5H_{11}N \\ C_5H_{11}N \end{matrix} > Pt < \begin{matrix} NC_5H_{11} \\ Cl \end{matrix} \right] Cl$$
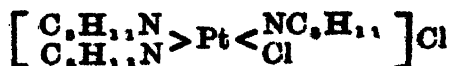
but evidence in favour of the above constitution is not available as the compound is insoluble in all the ionising solvents.

Interaction of tripropylamine and $PtCl_3.(C_2H_4)_3S_3$ leads to $PtCl_2.(C_2H_4)_2S_2$, the " thio " part being not replaced by the base. Only one atom of chlorine and the radicle (C_2H_4) are removed during the reaction. The compound may be regarded as a molecular one of the type of $AgCl.NH_3$ or may be constituted according to Werner, thus :—

$$\left[\{(C_2H_4)_2S_2\} > Pt < \begin{matrix} Cl \\ Cl \end{matrix} \right]$$
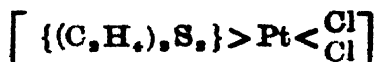
Diethylamine acting on $PtCl_3.(C_2H_4)_3S_3$ produces

(i) $PtCl_3. 2(C_2H_5)_2NH$

and (ii) $PtCl. (C_2H_5)_2NH. CH_3COCH_3.$
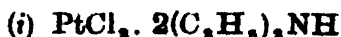
The former is a compound of the Werner type and may be represented thus—

$$\left[\begin{matrix} Et_2NH \\ Et_2NH \end{matrix} > Pt < \begin{matrix} Cl \\ Cl \end{matrix} \right]$$
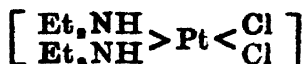
One molecule of the base of the above compound is replaced by one molecule of acetone when it is crystallised from that solvent giving rise to the compound (ii), which may consequently be represented as

$$\left[\begin{matrix} Et_2NH \\ (CH_3)_2CO \end{matrix} > Pt < \begin{matrix} Cl \\ Cl \end{matrix} \right]$$
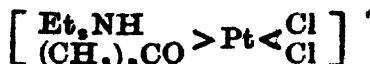
By the action of phenylenediamine on $PtCl_3(C_2H_4)_3S_3$, the compound $Pt_2Cl_3. 4 C_6H_4(NH_2)_2$ has been isolated.

In all the above cases it will be noticed that the original compound $PtCl_3.(C_2H_4)_3S_3$ is reduced by the action of the base, in most cases one atom of chlorine being eliminated. Direct proof in support of the view that one of the three chlorine atoms in the molecule is

more reactive in comparison with the other two could not be adduced as the compound $PtCl_2.(C_2H_4)_2S_2$ is insoluble in most organic or ionising media. The reactions with bases, however, indirectly support the assumption. Representing the compound by formula (I) the mechanism of reaction in most cases can be represented by the following scheme :—

$$\left[(C_2H_4)_2S_2 = Pt{<}^{Cl}_{Cl} \right] Cl \xrightarrow{\text{Reduction}} \left[(C_2H_4)_2S_2 {>} Pt{<}^{Cl}_{Cl} \right]$$
$$\text{(I)} \qquad\qquad\qquad\qquad\qquad \text{(II)}$$

$$\longrightarrow \left[{}^{B}_{B}{>}Pt{<}^{Cl}_{Cl} \right] \longrightarrow \left[{}^{B}_{B}{>}Pt{<}^{B}_{Cl} \right] Cl$$
$$\text{(III)} \qquad\qquad\qquad \text{(IV)}$$

$$\longrightarrow \left[{}^{B}_{B}{>}Pt{<}^{B}_{B} \right] Cl_2$$
$$\text{(V)}$$
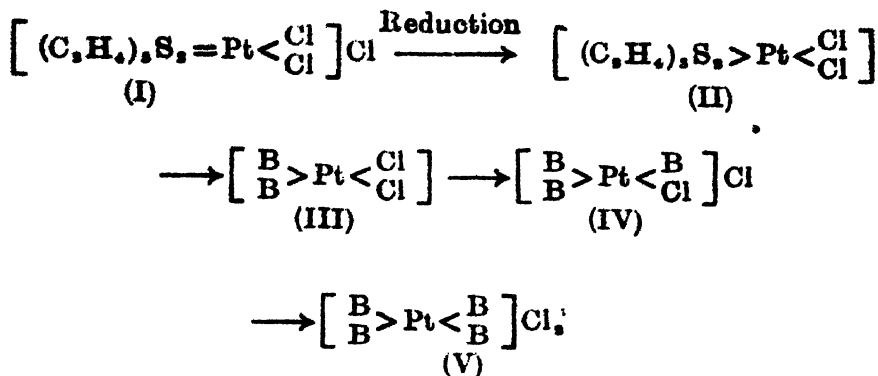
Compounds of the type (III) are found in (i) $PtCl_2.2(C_2H_5)_2NH$, and (ii) $PtCl_2.(C_2H_5)_2NH.CH_3COCH_3$. Type (IV) is represented by $PtCl_2.3C_5H_{11}N$, whereas (i) $PtCl_2.4C_6H_5CH_2NH_2$; (ii) $PtCl_2.4 C_5H_5N$. (iii) $PtCl_2. 4 NH_3$ and (iv) $PtCl_2.2C_2H_4(NH_2)_2$ are of the type (V).

The results obtained moreover show that in most cases the behaviour of $PtCl_2(C_2H_4)_2S_2$ towards bases is very similar to that of $PtCl_2.2Et_2S$ or $PtCl_2.2(PhCH_2)_2S$ (Roy Chowdhury, *private communication*) and that the parent substance is to be regarded as having the structure (I).

EXPERIMENTAL.

Action of Ammonia on $PtCl_2.(C_2H_4)_2S_2$.

The compound was suspended in water and ammonia was passed in for about one hour. The solid gradually went into solution and a white solid separated out which was found to be dithian. The liquid was filtered and the filtrate evaporated to dryness in a vacuum desiccator. The solid product was redissolved in a small quantity of water and precipitated by a little alcohol. This was filtered and found to be impure and was therefore rejected. To the filtrate a further quantity of alcohol was added when a brownish precipitate was obtained which was well washed with alcohol and dried in a vacuum desiccator.

The substance is very hygroscopic and did not melt when heated up to 200°. (Found: Pt, 58·61; Cl, 21·71; N, 16·98; S, absent. PtCl₂.4NH₃ requires Pt, 58·88; Cl, 21·26; N, 16·76 per cent.).

Conductivity Measurement of PtCl₂.4NH₃.

0·2108 gm. of the substance in 100 c.c. of water; hence concentration=M/159. Cell constant=0·095.

Strength of the soln.	Observed resistance.	Molecular conductivity.
M/159	56	=270 (approx).
M/1590	488	=315 (approx).

Thus molecular conductivity at about 1600 litres dilution (which may be taken to approach infinite dilution)=315, a value which is intermediate between the values for a ternary and a quarternary electrolyte.

Action of AgNO₃ on PtCl₂.4NH₃.

The substance was dissolved in water and precipitated by AgNO₃ in the cold. HNO₃ was not added as it might break up the complex. The result obtained, though low, is sufficiently convincing to indicate that both the chlorine atoms are ionisable. (Found: Cl, 19·42. PtCl₂.4NH₃ requires Cl, 21·26 (when both the chlorine atoms are ionisable) or Cl, 10·63 per cent. (when one chlorine atom is ionisable).

Action of Benzylamine.

The compound was just covered with benzylamine and heated on a water-bath for about half an hour. On cooling a semi-solid mass was obtained. It was several times washed with ether and boiling alcohol to remove dithian, benzylamine, etc., and then with little water followed by alcohol. The solid mass was then crystallised from boiling chloroform as fine silky, white crystals, m.p. 195°. (Found: Pt, 28·2; Cl, 10·9; N, 8·21. PtCl₂.4C₆H₅CH₂NH₂ requires Pt, 28·3; Cl, 10·2; N, 8·07 per cent.).

Action of Ethylenediamine.

The compound was just covered with an aqueous solution of ethylenediamine (about 1 per cent.) and the product was heated on a water-bath for 6-7 hours. It was then filtered and the filtrate,

on slow evaporation in a vacuum desiccator, yielded a crop of white crystalline substance, which was washed with a little water and alcohol and dried. It had no m.p. (Found: Pt, 41·10; Cl, 21·15; N, 9·77; S, 10·15. Pt_2Cl_6, $3C_2H_4(NH_2)_2.(C_2H_4)_2S_2$ requires Pt, 40·50; Cl, 22·10; N, 8·72; S, 10·15 per cent.).

The insoluble yellow portion was washed with hot water, alcohol, benzene and ether, and dried. (Found: Pt, 50·42; Cl, 17·96; S, 17·42. $PtCl_2$, $(C_2H_4)_2S_2$ requires Pt, 50·52; Cl, 18·39; S, 16·59 per cent.).

The compound was treated with an excess of ethylenediamine solution in water (1 : 5) and heated on a water-bath for about forty-five minutes. Dithian separated out during the reaction and was deposited on the colder part of the reacting vessel. This was then filtered off and the filtrate kept in a vacuum desiccator. The insoluble precipitate was found to be dithian. The mother-liquor on spontaneous evaporation yielded a crop of white crystals which were collected, washed with minimum quantity of water and alcohol and dried. The substance did not melt when heated up to 220°. (Found: Pt, 50·14; Cl, 18·30; N, 14·50. $PtCl_2.2C_2H_4(NH_2)_2$ requires Pt, 50·51; Cl, 18·39; N, 14·50 per cent.).

This compound is mainly obtained even if a large excess of 4 per cent. solution of ethylenediamine is used.

Action of Silver Nitrate on $PtCl_2.2C_2H_4(NH_2)_2$.

The substance was dissolved in water, as in the previous case without using nitric acid and treated with $AgNO_3$. The result obtained is low as before. (Found: Cl, 17·60. Calc. Cl, 18·39 (when both the chlorine atoms are ionisable).

Action of Pyridine on $PtCl_2(C_2H_4)_2S_2$.

The compound was treated with an excess of pyridine and heated on a water-bath for about eight hours. The liquid was then filtered off and the solid residue washed with hot pyridine two or three times. The filtrates, on evaporation, yielded transparent white crystals which were washed with chloroform to remove dithian. The substance was recrystallised from pyridine, washed with chloroform and dried. It turned yellow above 140° but did not melt. (Found: Pt, 38·1; Cl, 11·7; N, 8·84. $PtCl_2.4C_5H_5N$ requires Pt, 38·50; Cl, 12·19; N, 9·62 per cent.).

Ionisability of $PtCl_2.4C_5H_5N$.

(a) *Conductivity Method.—*

Concentration of the solution, M/1221 ;

Resistance found $=420$; Cell constant $= \cdot 095$

Hence, Molecular conductivity at 1221 litres dilution$=270$, *i.e.*, the substance is a ternary electrolyte.

(b) *Precipitation Method.—*

The substance was dissolved in water as in previous cases without using nitric acid. The result was low. (Found: Cl, 11·24. Calc. Cl, 12·19 per cent.).

The portion insoluble in pyridine was several times extracted with hot chloroform. The chloroform extract on evaporation gave shining yellow crystals which were filtered and dried. These had no m. p. (Found: Pt, 46·85, 46·3; Cl, 17·01; N, 6·50. $PtCl_2,2C_5H_5N$ requires Pt, 46·00; Cl, 16·75; N, 6·60 per cent.).

The portion insoluble in chloroform was then washed several times successively with warm water, alcohol, chloroform, benzene and alcohol, and dried. No m.p. (Found: Pt, 40·52; Cl, 26·1; N, 5·85; C, 24·85; H, 2·18. Pt_2Cl_7. $4C_5H_5N$ requires Pt, 40·8; Cl, 26·19; N, 5·86; C, 25·09; H, 2·09 per cent.).

Action of Dimethylaniline.

The compound was treated with an excess of dimethylaniline and heated on a water-bath for about an hour. The mass became greenish blue. It was filtered and the solid residue washed several times with alcohol, water, alcohol and benzene and dried. The product in the filtrate could not be isolated in a pure condition. (Found: Pt, 49·93; Cl, 18·01; N, 3·01. $PtCl_2,C_6H_5N(CH_3)_2$ requires Pt, 50·40; Cl, 18·85; N, 3·61 per cent.).

Action of Piperidine.

The compound was digested with an excess of piperidine on a water-bath for half an hour. A semi-solid mass was obtained which, on treatment with excess of ether, gave a crystalline compound. This was filtered and washed thoroughly with ether and alcohol and dried in a desiccator. The substance did not melt when heated up to 200°. (Found: Pt, 37·8; Cl, 13·51; N, 8·89. $PtCl_2,3C_5H_{11}N$ requires Pt, 37·4; Cl, 13·6; N, 8·06 per cent.).

Action of Tripropylamine.

The compound was digested with excess of tripropylamine on a water-bath for twelve hours. A yellowish green pasty mass was obtained. This was filtered, washed with water, alcohol, ether, benzene and chloroform, and the resulting yellow mass dried. (Found: Pt, 50·57; Cl, 18·31; S, 16·84. $PtCl_2(C_3H_4)_2S_2$ requires Pt, 50·52; Cl, 18·89; S, 16·59 per cent.).

Action of Diethylamine.

The compound was refluxed with an excess of diethylamine on a water-bath for three hours. It was then filtered and the solid residue washed several times with boiling alcohol, benzene and ether. The residue was then digested with chloroform and the chloroform solution on spontaneous evaporation yielded white crystals which were dried in a desiccator. (Found: Pt, 46·95; Cl, 17·63. $PtCl_2$, $2(C_2H_5)_2NH$ requires Pt, 47·53; Cl, 17·14 per cent.).

When the above substance is recrystallised from hot acetone, a shining yellow crystalline substance containing acetone is obtained. (Found: Pt, 50·18; Cl, 18·04; C, 21·52; H, 5·02*. $PtCl_2$. $(C_2H_5)_2$ NH, $(CH_3)_2CO$ requires Pt, 49·12; Cl, 17·88; C, 21·16; H, 4·35 per cent.).

Action of p-Phenylenediamine.

The compound was treated with an aqueous solution of p-phenylene diamine hydrochloride and heated on a water-bath. The violet insoluble portion was filtered, washed several times with water and alcohol and dried. The product in the filtrate could not be isolated in a pure state. (Found: Pt, 42·43; Cl, 11·04. $PtCl_2$. $4C_6H_4(NH_2)_2$ requires Pt, 42·03; Cl, 11·47 per cent.).

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* Percentage of hydrogen came rather high since the substance was mixed with copper oxide before combustion".

Reaction of Diazonium Salts with Hydroxymethylen cycloHexanones and Cyclic β-Diketones.

By Hemendra Kumar Sen and Sisir Kumar Ghosh.

It was observed by one of us (*J. Chem. Soc.*, 1915, **107**, 1347) that in a conjugated double bonded system of the type $\ominus=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}\cdot R$, the ethylenic linking is more reactive than the carbonyl group. Thus, the action of cyanacetamide on hydroxymethylene *cyclo*hexanones was shown to proceed in the following way giving rise to quinoline derivatives :—
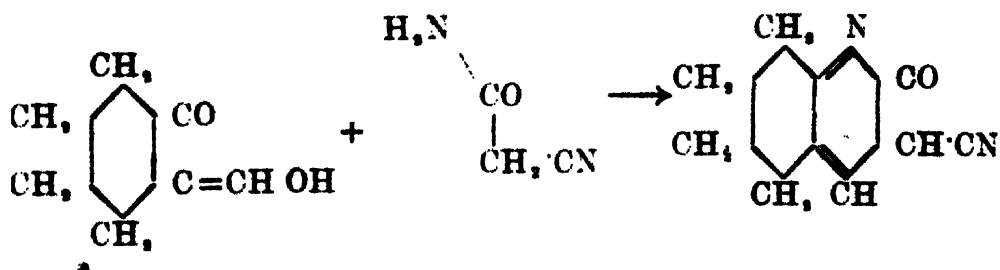
Burdhan suggested, however, (Thesis for the D.Sc. degree, Calcutta University, 1924) that the reaction above might also be explained as well by assuming the presence of a keto-aldehyde phase in hydroxymethylene *cyclo*hexanone in which the aldehyde group is naturally expected to be more reactive than the keto, thus leading to the formation of a quinoline derivative and not an *iso*quinoline one as would be the case if the keto group were more reactive. But this view of Burdhan's is rendered improbable by a recent work of Sen and Bose (*J. Indian Chem. Soc.*, 1927, **4**, 51) who found that the reactivity of a β-diketone with cyanacetamide tends to disappear where the chance of enolisation is least possible.

As in hydroxymethylene *cyclo*hexanone the enolisation is at the formyl group, and since quinoline derivatives are actually obtained by condensing them with cyanacetamide, it is not necessary to accept Burdhan's view to explain this course of reaction. The ordinary assumption that hydroxymethylene ketones are permanently enolised β-diketones, if true for open-chain compounds, is, however,

not true for cyclic hydroxymethylene ketones. The existence of a considerable proportion of a keto-aldehyde phase along with the keto-enol in the latter, is proved in the present work. The bromine titration method (an account of which will be very shortly communicated) also points to the same conclusion. When methyl iodide is allowed to react with the sodium salt of hydroxymethylene *cyclo*-hexanone in absolute alcoholic solution, (i) O-methyl ether of hydroxymethylene *cyclo*hexanone, and (ii) *ortho*-methyl *cyclo*hexanone are obtained. Obviously, the chance of enolisation under the experimental condition is great, and as such the exclusive formation of the O-methyl ether should be expected. In reality, however, about 40 per cent. of the reaction product is *ortho*-methyl *cyclo*-hex· none. The presence, therefore, of a considerable proportion of the keto-aldehyde phase even in absolute alcoholic solution, must account for the formation of *ortho*methylcyclohexanone, unless indeed one assumes the wandering of the methyl group from oxygen to carbon.
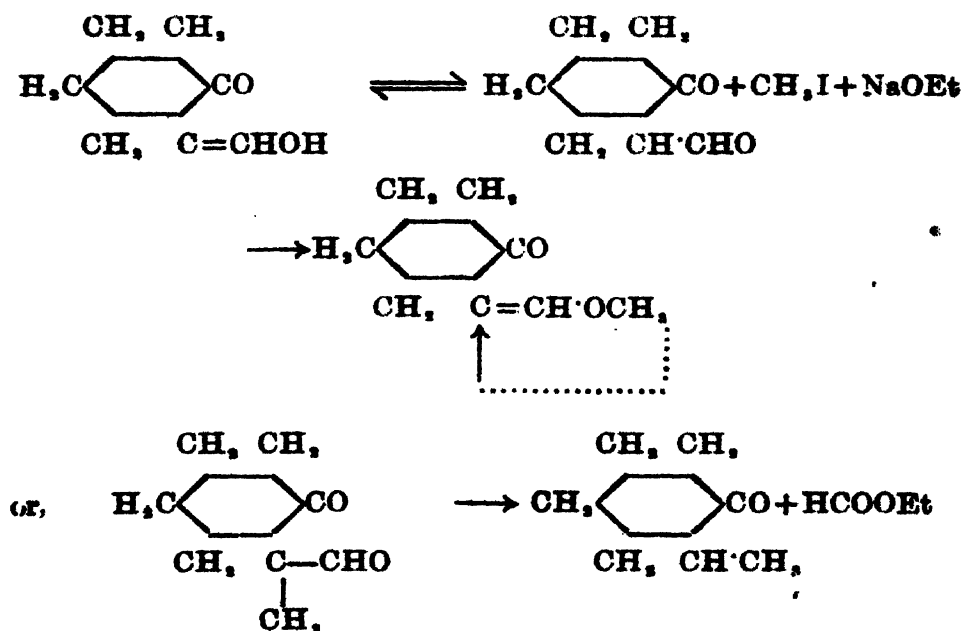
If, however, the sodium salt of hydroxymethylene *cyclo*hexanone is prepared by the addition of metallic sodium to the hydroxymethylene ketone in benzene suspension, the product obtained on methylation (also in benzene solution) gives on treatment with cold potash, *ortho*methylcyclohexanone as the main product which establishes the presence of a keto-aldehyde phase.

The presence of the keto-aldehyde in hydroxymethylene cyclo-hexanone is further evident from the following reaction which was next studied *in extenso*. When diazonium chloride reacts with hydroxymethylene cyclohexanone in presence of sodium acetate, the reaction product, obtained in nearly quantitative yield, is in a state of fairly good purity, and corresponds to a monophenylhydrazone of diketohexamethylene. Unfortunately, after the work had proceeded far we noticed that Coffey (*Abs. Chem. Soc., Lond.* 1923, (i), 808; *Rec. trav. Chim.*, 1923, **42**, 528) had already studied this particular case in this type of reaction, *i.e.*, the action of diazonium chloride on hydroxymethylene cyclohexanone. No doubt this took away much of the real interest of the subject, but on extending the reaction to acetyl and carbethoxy cycloketones, important differentiating properties of β-diketones and hydroxymethylene cycloketones were observed.

The action of diazonium chloride on hydroxymethylene cyclo-hexanone gives, as already stated, a monophenylhydrazone of diketo-cyclohexane (*cf.* Coffey); we have found that with the various hydroxy-methylene cycloketones and diazo salts, the monophenylhydrazones are invariably obtained. That they are monophenylhydrazones is established from the following two facts : —

(i) When they are heated for sometime with glacial acetic acid, a conversion analogous to Fischer's indole synthesis takes place, giving rise to carbazole derivatives.
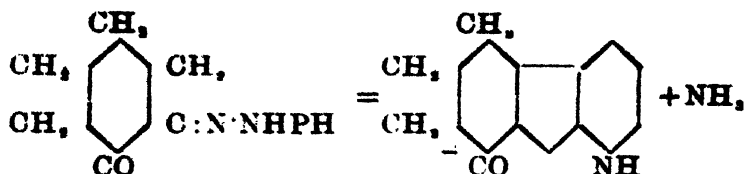
(ii) On heating the original reaction products with phenylhydra-zine, osazones are readily obtained. Thus mono-phenylhydrazone of diketohexamethylene yields the same osazone as was prepared by Kötz from oxycyclohexanone (*Abs.* 1913, i, 1201).

As is obvious, the formation of monophenylhydrazone from hydroxymethylenecyclohexanone and diazonium salts, necessitates the removal of the formyl group to give the necessary hydrogen for the formation of phenylhydrazone.

The reaction can be expressed as below :—

$$\begin{array}{c} CH_2 \quad CH_2 \\ H_2C \diagdown \quad \diagup CO \\ CH_2 \quad C \\ \quad \| \\ \quad CH \cdot OH \end{array} \rightleftharpoons \begin{array}{c} CH_2 \quad CH_2 \\ H_2C \diagdown \quad \diagup CO + Cl.N=N.Ph \\ CH_2 \quad CH \end{array}$$

$$\downarrow$$

$$\left[\begin{array}{c} CH_2 \quad CH_2 \\ H_2C \diagdown \quad \diagup CO \\ CH_2 \quad C-N=N.Ph \\ \quad | \\ \quad CHO \end{array} \right] \quad or \begin{array}{c} CH_2 \quad CH_2 \\ H_2C \diagdown \quad \diagup CO \\ CH_2 \quad C=N.N.Ph \\ \quad | \\ \quad CHO \end{array}$$

$$\Big\downarrow \text{EtOH, or } H_2O \qquad\qquad \Big\downarrow \text{EtOH, or } H_2O$$

$$\begin{array}{c} CH_2 \quad CH_2 \\ H_2C \diagdown \quad \diagup CO \\ CH_2 \quad C \end{array} \quad + \quad \begin{array}{c} HCOOEt \\ or \\ HCOOH \end{array}$$

$$N.NH.Ph$$
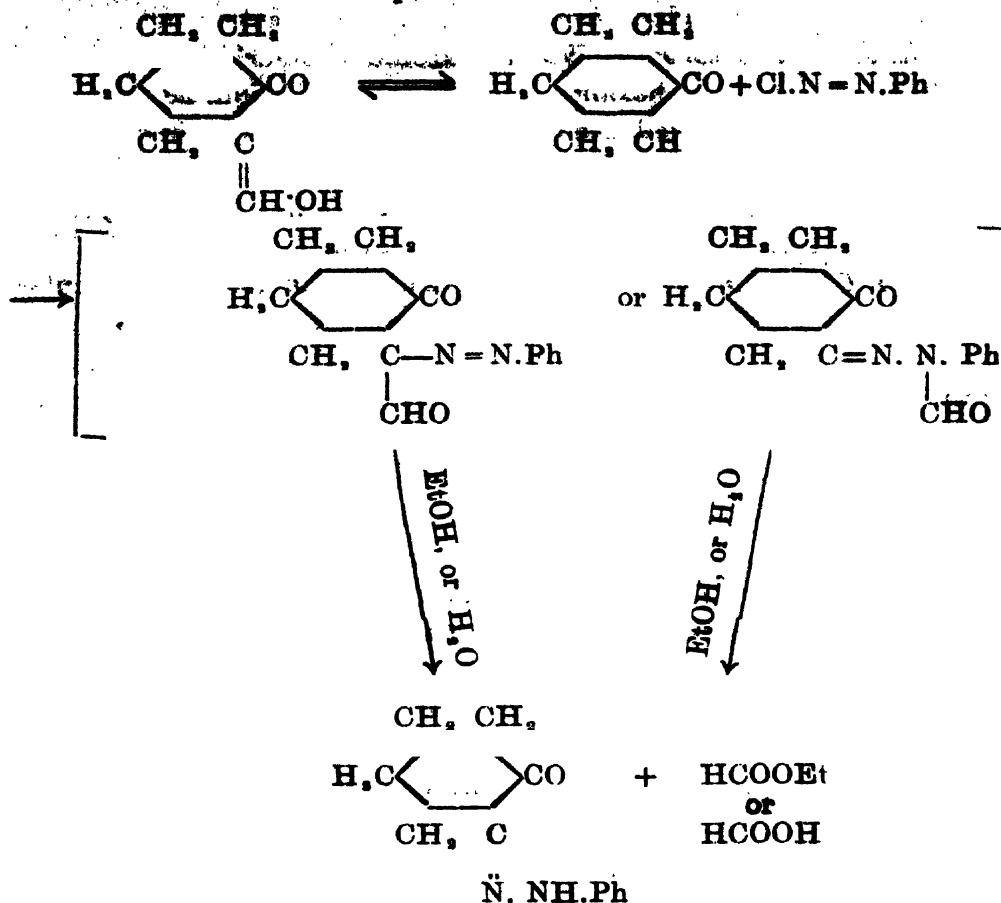
Very recently Benary, Meyer and Charisius have shown (*Ber.*, 1926, **59**, 109) that open-chain hydroxymethylene ketones react with diazobenzene chloride giving the following type of compounds :—

$$CH_3.CO.CH=CHOH \rightleftharpoons CH_3.CO.CH_2.CHO + Cl.N=N.Ph$$

$$\longrightarrow \left[\begin{array}{c} CH_3.CO.CH.CHO \\ | \\ N=N.Ph \end{array} \right] \longrightarrow \begin{array}{c} CH_3.CO.C.CHO \\ \| \\ N.NH.Ph \end{array}$$
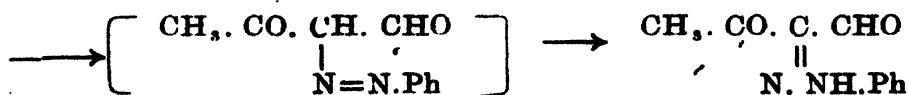
In these cases the formyl group is intact. That the formyl group is split off from hydroxymethylene *cyclo*hexanones under similar conditions is confirmed by analysis and the facts that (i) a distinct odour of ethyl formate is obtained as the reaction proceeds and that (ii) the filtrate from the reaction product gives a distillate which reduces mercuric chloride to mercurous chloride. The elimination of the formyl group, so peculiar in the case of cyclic hydroxymethylene ketones, can be explained thus : In open-chain hydroxymethy-

lene compounds there is hydrogen available for the formation of phenylhydrazones, whilst in cyclic hydroxymethylene ketones no such hydrogen is present, and as such if the tendency is to produce a hydrazone under the experimental conditions, the formyl group, by splitting off, supplies the hydrogen.* That they are hydrazones has been conclusively proved alike by our own work as also by previous workers (V. Meyer, *Ber.*, 1888, **21**, 11; Japp and Klingemann, *J. Chem. Soc.*, 1888, **53**, 519; Pechmann, *Ber.*, 1892, **25**, 3190; *Ber.*, 1894, **27**, 219; Favrel, *Compt. rend.*, 1901, **132**, 41; *Compt. rend.*, 1892, **134**, 1312; Rabischogon, *Bull. Soc. Chim.*, 1904, (iii) **31**, 76; Dimroth, *Ber.*, 1908, **41**, 4012, etc.). The tendency to form phenylhydrazones in such cases is so great that CO_2 and acetyl group are split off respectively from alkylacetoacetic acids and alkylacetoacetic esters (*cf.* Japp and Klingemann, *loc. cit*).

$$
\begin{array}{c}
CH_3.CH.COOH \\
| \\
CH_3.CO
\end{array}
+ Cl.N:N\cdot Ph =
\begin{array}{c}
CH_3.C = N.NHPh \\
| \\
CH_3 CO
\end{array}
+ CO_2 + HCl
$$

$$
\begin{array}{c}
CH_3.CH.CO_2Et. \\
| \\
CH_3.CO
\end{array}
+ Cl.N:N.Ph =
\begin{array}{c}
CH_3.C.CO_2Et. \\
|| \\
N.NH.Ph
\end{array}
+ CH_3.CO_2H + HCl
$$
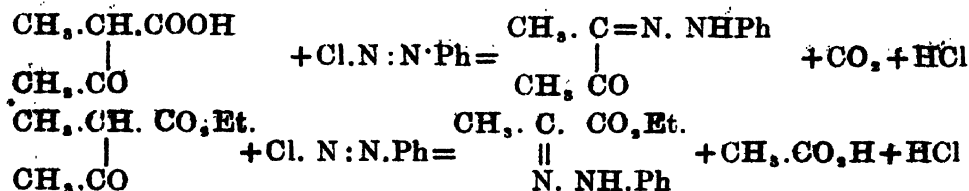
Mention has already been made that the course of reaction of diazonium chlorides with hydroxymethylene *cyclo*hexanones is different from that with other cyclic β-diketones, such as acetyl *cyclo*hexanones. If this were not so, the same hydrazone would be obtained whether one started with hydroxymethylene *cyclo*hexanone or acetyl *cyclo*hexanone (or *cyclo*hexanone carboxylate). The reaction probably proceeds, however, in the following way :—
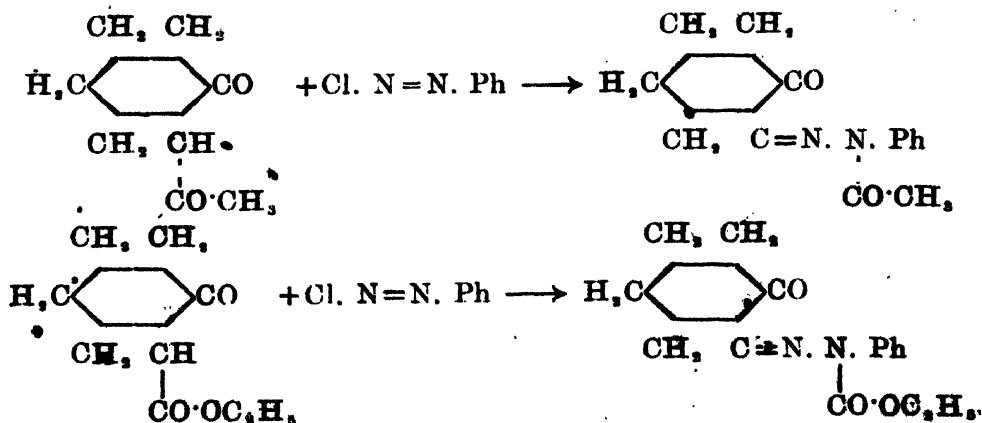
* The question may arise, why is the resulting compound a hydrazone and not an azo-derivative?

This point is at present under investigation and is expected to be elucidated by preparing the acetylphenylhydrazone of diketohexamethylene.

The explanation of the non-elimination of the acyl group here, as distinct from the formyl group in hydroxymethylene cyclohexanone, probably lies in the fact that the asymmetrical formyl-phenylhydrazone is unknown doubtless on account of its instability, whereas acetyl-phenylhydrazone and carbethoxy-phenylhydrazone are stable. No carbazole derivatives have been obtained from these even on prolonged boiling with acetic acid, probably because of the difficulty of obtaining the hydrogen necessary for the elimination of ammonia. A further peculiarity of these acyl phenylhydrazones is their solubility in dilute alkali and precipitation on acidification without any decomposition. The behaviour is difficult to explain unless one assumes that the ketonic group left free enolises. Sodium carbonate solution does not dissolve them. In the case of the monophenylhydrazone of diketocyclohexanes formed by the action of diazo salts with hydroxymethylene-cyclohexanones this solubility in alkali is extremely small although a little does dissolve. Probably the absence of any strongly acidic group in the compound accounts for this depreciated solubility. The question, however, has to be left open for the present.

A fact of considerable interest has been noticed in one or two cases of these condensation products which points to the existence of isomers (cf. J. pr. Chem., 1892, (ii) 46, 579; 1893, 47, 591, Ber., 1897, 30, 1965). Thus the monotolyl hydrazone of 1-methyl-2 : 8 diketocyclohexane exists in two forms, one melting at 91-93°, and the other at 117-118°. The possibility of the existence of isomers is seen from the following representation :—

$$
\begin{array}{ccc}
& \text{CH}_3 & \\
& | & \\
\text{CH}_2 & \text{CH} & \\
\text{H}_2\text{C} \diagdown \quad \diagup \text{CO} & \text{and} & \\
\text{CH}_2 & \text{C} & \\
& || & \\
\text{N. NH. C}_6\text{H}_4\text{. CH}_3 &
\end{array}
$$
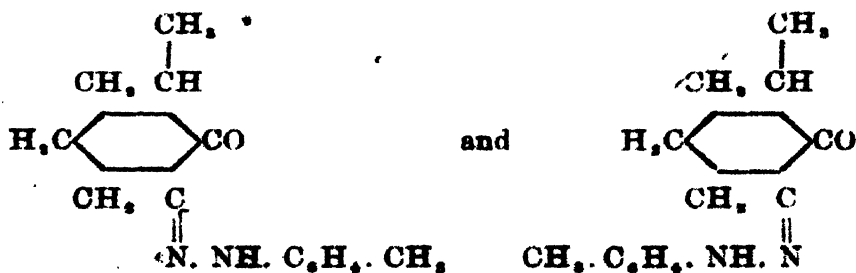
In other instances, although isomers of distinctly different melting points have not been isolated, their indifferent melting points would lead one to suspect the existence of these as mixtures.

EXPERIMENTAL.

*1-Hydroxymethylene-*cyclohexane*-2-one and Diazobenzene Chloride: Formation of* cyclo*Hexane-1 : 2-dione-mono-phenyl hydrazone.*

1-Hydroxymethylenecyclohexane-2-one was obtained by the usual method of Borsche (A., 1910, i, 880).

In a beaker of about 600 c.c. capacity, 1-hydroxymethylene-cyclohexane-2-one (10 g.) was mixed with a saturated solution of sodium acetate (25 g.). The turbid solution was made clear by the addition of a sufficient quantity of alcohol and allowed to cool in a bath of freezing mixture. After it had cooled to 0°, a diazo-solution obtained from one molecular equivalent of freshly distilled aniline (7.8 g.) was added to it in small quantities with vigorous stirring. The operation was completed in the course of about half an hour when a yellow precipitate was obtained. A distinct odour of ethyl formate was noticed as the reaction proceeded. The yellow precipitate was then rapidly filtered and the filtrate was preserved for further treatment as will be described below. The precipitate was thoroughly washed with water to free it from sodium acetate and other adhering impurities. This was then dried and weighed, a nearly theoretical yield being obtained. It was found convenient to crystallise it from hot glacial acetic acid in which it is moderarely soluble. It was found also expedient to boil up with animal charcoal before crystallisation as otherwise the colour of the crystals appeared to be somewhat dirty. The crystals were beautiful, lustrous and reddish-yellow in colour and melted at 181°-185°. (Found : N, 14·10; C, 70·99 ; H, 7·13. $C_{12}H_{14}ON_2$ requires N, 13.86 ;C, 71·28; H, 6·93 per cent.)

This was moderately soluble in most of the organic solvents. It also slightly dissolves in dilute alkali.

Confirmation of the Presence of Ethyl Formate in the Reaction Mixture.

The filtrate mentioned above was distilled on a water-bath and the distillate was collected between 53° and 80°. In the distillate, a strong odour of ethyl formate was noticed. On addition of a solution of mercuric chloride to a little of it at first a white turbidity was formed which on standing settled down to a white precipitate

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due to the formation of mercurous chloride. The smallness of the precipitate was perhaps due to the presence of only a small quantity of ethyl formate.

1-Keto-tetrahydro-carbazole.

A few grams of the monophenylhydrazone obtained were dissolved in an excess of glacial acetic acid and heated under reflux for one hour. When cold the solution was diluted with water when a brownish white precipitate was obtained. This was filtered and recrystallised from hot 50 per cent acetic acid. Greyish white needles melting at 168° were obtained. (Found: N, 7·78. $C_{12}H_{11}ON$ requires N, 7·5 per cent.).

cycloHexane-1:2-dione-diphenylhydrazone.

The monophenylhydrazone obtained, an equivalent quantity of phenylhdrazine hydrochloride, and sodium acetate in excess were heated on a water-bath for one hour in alcoholic solution under reflux. Sodium chloride separated, which dissolved on the addition of water, and a yellow precipitate was obtained. This was thoroughly washed and recrystallised from hot alcohol by the addition of a few drops of water. Fine yellow coloured crystals, m.p. 15ɔ°-154°. (Found: N. 19·36; C, 73·87; H, 7·08. $C_{18}H_{20}N_4$ requires N, 19· 18; C, 73·98; H, 6·84 per cent.).

This compound was found to be identical with that obtained by Kötz (cf. A., 19l3, i, 1201) by the action of phenylhydrazine on 2-hydroxycyclohexane-1-one prepared by the hydrolysis of chlor-2-cyclohexanone-1. A mixture of Kötz's compound and ours showed no lowering of melting point. While preparing Kötz's componnd it was found that the same could be prepared much easier in the following way. Instead of hydrolysing chlor-2-cyclohexanone-1 by K_2CO_3 and then treating the 2-hydroxycyclohexanone-1 thus isolated with phenylhdrazine, the osazone could be obtained by hydrolysing 2-chloro-cyclohexanone with KOH solution and treating it with phenylhydrazine after acidification.

1-Hydroxymethylene-cyclohexane-2-one and p-Diazotoluene Chloride: Formation of cycloHexane-1:2-dione-mono-p-tolylhydrazone.

The condensation product was obtained as previously using p-toluidine for diazotisation, the yield being 97%. After recrystalli-

sation from hot glacial acetic acid and also boiling with animal charcoal, it was obtained as yellow crystals melting at 190.° (Found: N, 13·30 ; C, 72·51 ; H, 7·60. $C_{13}H_{13}ON_2$ requires N, 12·96 ; C, 72·22 ; H, 7·41 per cent.)

1-Keto-tetrahydro-3-methyl-carbazole.

This was obtained as before by heating in an excess of glacial acetic acid the monotolyl-hydrazone obtained as above for one hour. After recrystallisation by boiling with animal charcoal from 50 per cent acetic acid, it was obtained as colourless flakes sintering at 192° and melting at 194° (Found: N, 7·29. $C_{13}H_{13}ON$ requires N, 7·03 per cent.).

cycloHexane-dione-1-phenyl-2-p-tolylhydrazone.

It was obtained as previously by the action of phenylhydrazine hydrochloride and excess of sodium acetate on cyclohexane-1:2-dione-mono-p-tolylhydrazone. When recrystallised from alcohol diluted with a few drops of water it was obtained as yellow coloured crystals sintering at 145° and melting at 150°. The melting point was not very sharp even after two or three crystallisations. (Found: N, 18·72; C, 74·08; H, 7·60. $C_{19}H_{22}N_4$ requires N, 18·29; C, 74·50; H, 7·18 per cent.).

1-Hydroxymethylene-cyclohexane-2-one and Diazo-p-nitrobenzene Chloride: Formation of cycloHexane-1:2-dionemono-p-nitrophenyl hydrazone.

The condensation was effected as previously using diazotised p-nitraniline. The product was crystallised from hot glacial acetic acid in which it is sparingly soluble. The crystals were obtained as dark brown needles, melting between 228° and 230° blackening a few degrees earlier (223°). The yield in this case was nearly 98 per cent. (Found: N, 17·32. $C_{12}H_{13}O_3N_3$ requires N, 17·00 per cent.).

It is insoluble in most of the organic solvents except in glacial acetic acid in which it is sparingly soluble. It also slightly dissolves in dilute alkali.

1-Keto-tetrahydro-3-nitro-carbazole.

This was obtained as previously by boiling the phenylhydrazone obtained as above with an excess of glacial acetic acid for two hours

and a half. This was recrystallised from hot alcohol. Light -brown crystals sinter at 209°. and melt at 212°. (Found: N, 12·85. $C_{18}H_{16}$ O_2N_2 requires N, 12·17 per cent.).

cycloHexane-dione-1-p-nitrophenyl-2-phenylhydrazone.

CH² CH₂

H_2C ⟨⟩ $C=N$. NH. C_6H_5

CH₂ $C=N$. NH. C_6H_4. NO₂[1:4]
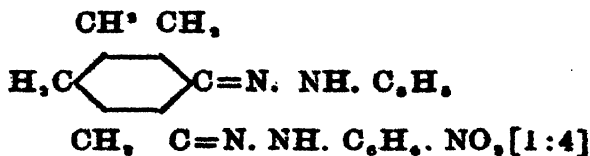
Phenylhydrazine hydrochloride dissolved in alcohol was mixed with a saturated solution of sodium acetate and to this was added the phenylhydrazone obtained as above which remained in suspension owing to its insolubility in alcohol. This was heated on the water-bath under reflux for 2 hours when the colour of the suspended phenylhydrazone was found to have changed from reddish-brown to scarlet-red. This was filtered, washed with water, and crystallised from hot alcohol in which it was sparingly soluble. It was obtained as scarlet coloured crystalline powder having m.p. 215°—217°. It is insoluble in most other organic solvents. (Found: N, 20·53. $C_{18}H_{18}N_4O_2$ requires N, 20·77 per cent.).

1-Hydroxymethylene-3-methyl-cyclohexane-2-one and Diazobenzene Chloride: Formation of 3-methyl-cyclohexahe-1:2-dionemonophenylhydrazone.

1-Hydroxymethylene-3-methyl*cyclo*hexane-2-one was obtained in the usual way by condensing together o-methyl-*cyclo*hexanone and *iso*amyl formate. The liquid boils at 112°—114°/40 mm.

The condensation was effected in the usual way between 1-hydroxymethylene-3-methyl*cyclo*hexane-2-one and diazobenzene chloride. The yield in this case was somewhat less (about 85 per cent.). As this was found to be a low melting substance it was crystallised in the following way:—It was first dissolved in alcohol, boiled with animal charcoal and filtered. Then the solution was cooled and drops of water added till turbid. On keeping the solution at that condition for sometime beautiful yellow crystals appeared which melted with following characteristics. It began to sinter at 88°, then partly melted at 91°, got turbid, and the turbidity cleared at 131°. Even after crystallisation for three times no improvement was noticed in its m.p. Its analyses for nitrogen,

carbon and hydrogen point, however, to its homogeneous composition. It seems, therefore, to be a mixture of two isomers as already mentioned (*loc. cit.*). (Found: N, 13·08 ; C, 71·90; H, 7·68. $C_{13}H_{13}ON_3$ requires N, 12·96; C, 72·21; H, 7·46 per cent.).

It is extremely soluble in most of the organic solvents. It also slightly dissolves in dilute alkali. It is very unstable. The well-shaped crystals when kept in a sample tube gets resinified within a fortnight.

1-*Keto-2-methyl-tetrahydro-carbazole.*

This was obtained as usual by heating the monophenylhydrazone in an excess of glacial acetic acid for about ten minutes. If it is boiled for a longer time it gets charred. On cooling it was diluted with water when a brownish black precipitate was obtained. This gave colourless crystals, m.p. 171°-73° after boiling with animal charcoal in alcohol. It can also be crystallised from 50 per cent. acetic acid. (Found: N, 7·06 ; C, 78·08; H, 6·81. $C_{13}H_{13}NO$ requires N, 7·03 ; C, 78·38; H, 6·53 per cent.).

3-*Methylcyclohexane-1:2-dione-diphenylhydrazone.*

This was obtained as usual by heating phenylhydrazine hydrochloride, excess of sodium acetate and monophenylhydrazone prepared as above, in an alcoholic solution for half an hour. This was filtered and recrystallised from alcohol by adding a few drops of water. Fine yellow crystals, m. p. 151°—153°. (Found: N, 18·55; C, 74·39; H, 7·26. $C_{19}H_{21}N_4$ requires N, 18·3 ; C, 74·50; H, 7·19 per cent.).

1-*Hydroxymethylene-3-methyl-cyclohexane-2-one and p-Diazo-toluene Chloride : Formation of 3-methyl-cyclohexane-1:2-dione-mono-p-tolylhydrazone.*

The condensation was effected in the usual way, the yield being about 85 per cent. It was crystallised in the same way as in the case of monophenyl-hydrazone. But while crystallising, two products having different melting points were isolated. At first the crude product was dissolved in alcohol and boiled with animal charcoal. This was filtered and to the cold solution drops of water were added till the solution was turbid. On standing crystals separated. This was filtered and the filtrate preserved. The crystals so obtained were recrystallised again and again for 3 or 4 times from dilute alcohol. From this, yellow needle-shaped crystals m.p. 117°.

180° were obtained. On the addition of more water to the mother-liquor after first filtration, a product was obtained which on recrystallisation from alcohol diluted with water melted at 91°—93°. On analysis the two were found to have identical composition and hence they seemed to be isomers. [Found: (i) m.p. 91°—93°, N, 12·47; C, 72·61; H, 8·30; (ii) m.p. 117°—118°, C, 72·69; H, 8·32. $C_{18}H_{18}ON_2$ requires N, 12·17; C, 73·04: H, 7·88 per cent.).

This is also very soluble in most organic solvents. It slightly dissolves in dilute alkali. This is also unstable, as after keeping it for more than one month in a sample tube, tarry matters separated.

1-Keto-2-methyl-tetrahydro-3-methylcarbazole.

This was obtained as before by boiling the tolylhydrazone in an excess of glacial acetic acid for ten minutes. Longer heating chars the product. When cold, it was precipitated with water and the product was recrystallised from 50 per cent. acetic acid after boiling with animal charcoal. Colourless crystals, m.p. 195°. It can also be crystallised from 50 per cent. alcohol. (Found: N, 6·88; C, 78·89; H, 7·22. $C_{14}H_{15}ON$ requires N, 6·57; C, 7–·87; H, 7·04 per cent.).

3-Methyl-cyclohexane-1:2-dione-1-tolylhydrazone-2-phenylhydrazone.

This was obtained as previously by heating the alcoholic solution of the tolylhydrazone prepared, phenylhydrazine hydrochloride and sodium acetate on a water-bath for about half an hour. The product obtained when crystallised from hot alcohol came down in beautiful yellow crystals, m.p. 158°-159°. (Found: N, 17·63. $C_{20}H_{24}N_4$ requires N, 17·50 per cent).

1-Hydroxymethylene-3-methyl-cyclohexane-1:2-dione and β-Diazonaphthalene Chloride: Formation of 3-Methyl-cyclohexane-1:2-dione-naphthylhydrazone.

The condensation of the two was effected in the same way as before, using diazotised β-naphthylamine (yield about 55% of the theoretical).

The condensation product so obtained contained much tarry matters; so it was at first dried in a vacuum desiccator and then treated with petroleum ether in which the tarry matters dissolved. Then the product was crystallised from cold methyl alcoholic solution diluted with a few drops of water. The crystals obtained were

reddish yellow in colour and melted between 85° and 86°. It is fairly soluble in most organic solvents and slightly in dilute alkali. It is also unstable, tarry matters being separated from well-defined crystals after sometime. (Found : N, 10·90. $C_{17}H_{18}ON_2$ requires N, 10·53 per cent.).

1-Keto-2-methyl-tetrahydro-naphtho-carbazole.

This was obtained as previously by heating the naphthyl-hydrazone in an excess of glacial acetic acid for ten minutes. The product obtained was crystallised from 50 per cent. acetic acid when greyish white crystals were formed melting at 225° blackening at 212°. (Found : N, 5·39. $C_{17}H_{14}ON$ requires N, 5·62 per cent.).

The osazone has not been obtained by the further action of phenylhydrazine hydrochloride in presence of sodium acetate.

1-Acetyl-cyclohexane-2-one and Diazobenzene Chloride : Formation of cycloHexane-1 : 2-dione-mono-acetylphenylhydrazone.

1-Acetyl-cyclohexane-2-one was prepared according to Lesser's method (Bull. Soc. Chim., 1900, (iii) 23, 370.)

1-Acetyl-cyclohexane-2-one (3 g.) dissolved in a little alcohol was mixed with a saturated solution of sodium acetate (15 g. in 25 c.c. of water) and the turbidity that ensued was just dissolved by the addition of a further quantity of alcohol. The solution was then allowed to cool in a freezing bath. A diazobenzenechloride solution was prepared from an equivalent quantity of freshly distilled aniline. The diazo solution was then poured into the ice-cooled acetylcyclohexanone solution adding a small portion at a time and stirring well the mixtures with a glass rod. Contrary to previous experience, instead of a crystalline precipitate the mixture turned into an emulsion from which an oil separated at the end of the reaction. The reaction mixture was found to solidify on keeping in the freezing bath for 2-3 hours and then at the room temperature overnight. The solid mass was next morning filtered and washed with a little rectified spirit which dissolved the tarry matters. The yield was nearly 60%. It could be obtained pure from hot 50% acetic acid after three crystallisations, but it was found convenient to purify it as follows :—It was reprecipitated by acidification with acetic acid from its solution in dilute alkali in which it was found to dissolve (loc. cit). The reprecipitated substance was then dissolved in 50% acetic acid and boiled with animal charcoal. The filtered solution,

on cooling, deposited crystals which were again crystallised from acetic acid. The substance was obtained as fine yellow plates, m.p. 159°-161°. (Found: N, 11·60. $C_{16}H_{18}O_2N_2$ requires N, 11·48 per cent.).

It dissolves in acetic acid, ethyl alcohol, methyl alcohol etc., but is insoluble in benzene, petroleum ether and chloroform. It dissolves completely in dilute alkali from which it can be recovered unchanged by acidification.

1-*Acetyl*-cyclohexane-2-one and p-*Diazotoluene Chloride* : *Formation of* cyclo*Hexane*-1 : 2-*dione-mono-acetyl-tolylhydrazone*.

The condensation was effected in the same way as above using p-toluidine. In this case also an oil separated which on keeping overnight solidified (yield 60% of the theoretical). This was crystallised in the same way as above by first dissolving in dilute alkali and the product after acidification was thrice crystallised from 50% acetic acid when beautiful yellow plates were obtained melting at 151°-153°. (Found: N, 10·95. $C_{15}H_{18}O_2N_2$ requires N, 10·85 per cent.).

It also dissolves in dilute alkali from which it can be obtained unchanged by acidification. It is fairly soluble in most organic solvents.

3-*Methyl*-1-*acetyl*-cyclohexane-2-one and Diazobenzene *Chloride* : *Formation of* 3-*Methylcyclohexane*-1 : 2-*dione-mono-acetylphenyl-hydrozone*.

3-Methyl-1-acetyl-*cyclo*hexane-2-one was prepared according to Lesser's method. From 50 gms. of o-methyl-*cyclo*hexanone only 9 g. of 3-methyl-1-acetyl-*cyclo*hexane-2-one were obtained. The liquid boils at 100°-105°/15 mm.

The condensation was effected in the same way as above. The yield was the same as in the former case. An oil separated which on keeping overnight solidified. It is best crystallised by thrice dissolving in 50% acetic acid. The method of dissolving in dilute alkali and reprecipitating with acetic acid was not suitable. Yellow plates, m.p. 137°-140°, were obtained. (Found: N, 10·90. $C_{15}H_{18}O_2N_2$ requires N, 10·35 per cent.).

This also dissolves in dilute alkali and can be obtained unchanged by acidification. It is soluble in most organic media but is insoluble in petroleum ether.

3-Methyl-1-acetyl-cyclohexane-2-one and p-Diazotoluene Chloride : Formation of 3-Methyl-cyclohexane-1:2-dione-mono-acetyltolylhydrazone.

The condensation product was obtained as previously as an oil at first which, on keeping over-night, solidified. The yield was the same as before. This is best crystallised from hot benzene, when it is obtained as light yellow crystals, m.p. 117°-120°. (Found : N, 10·15. $C_{16}H_{20}O$ N requires N, 10·28 per cent.).

It also dissolves in dilute alkali from which it can be precipitated unchanged by acid. It is soluble in most of the organic solvents.

1-Carbethoxy-cyclohexane-2-one and Diazobenzene Chloride : Formation of cycloHexane-1:2-dione-mono-carbethoxy-phenylhydrazone.

1-Carbethoxy-cyclohexane-2-one was prepared according to the method of Kötz, (A., 1905, 346). The condensation was effected as usual by adding the diazo-solution to ethylcyclohexanonecarboxylate in a saturated solution of sodium acetate. At the end of the reaction an oil separated, which on keeping overnight solidified. This is best crystallised by first dissolving in dilute alkali and then precipitating by acidification. After two crystallisations from 50% acetic acid (using animal charcoal) long needle-shaped light yellow crystals were obtained, m.p. 90°-92°. (Found : N, 10·11. $C_{15}H_{18}O_3N_2$ requires N, 10·22 per cent.). It is moderately soluble in most of the organic solvents.

1-Carbethoxy-cyclohexane-2-one and p-Diazotoluene Chloride : Formation of cycloHexane-1:2 dione-mono-carbethoxytolylhydrazone.

The condensation was effected as usual. The product was an oil which afterwards solidified. It was found convenient to crystallise it from methyl alcohol diluted with a few drops of water. The substance was obtained as brown crystals, m.p. 97°-99°. (Found : N, 9·86. $C_{16}H_{20}O_3N_2$ requires N, 9·72 per cent.).

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Variation of the Charge of Colloidal Particles. Part II. Effect of Dilution and of Non-electrolytes on the Charge and its Variation with Concentrations of Electrolytes.

By Jnanendra Nath Mukherjee, Subodh Gobinda Chaudhury
and Satya Prosad Rai Choudhuri.

Discussions on the influence of external factors on the coagulating power of an electrolyte centre round certain assumptions regarding the electrical charge of the colloidal particles such as :

(a) that the charge does not change on dilution,

(b) that a given rate of coagulation of the same sol by different electrolytes is characterised by a definite value of the potential of the double layer. (Some authors still hold that coagulation takes place at the iso-electric point).

Powis (*Zeit. physical. Chem.*, 1915, **89**, 186) postulated that coagulation takes place when the potential falls below a critical value. But he himself observed for arsenious sulphide sol (*J. Chem. Soc.*, 1916, **109**, 734) that this is not always so. These measurements are not so reliable as those he carried out with oil emulsions, for he used the procedure suggested by Burton which is undoubtedly erroneous (Mukherjee, *Thesis*, (1921), also *Proc. Roy. Soc.*, 1923, **103A**, 102.). Even the fundamental assumption of a direct relationship between the rate of migration of the particles in an electric field which is taken as a measure of the potential of the double layer and its stability is untenable (for a full criticism see Mukherjee, *Thesis, loc. cit.*, Mukherjee and Chaudhury, *J. Indian Chem. Soc.* 1925, **2**, 296). Recently Dhar and his co-workers in a number of papers have attempted to classify so-called suspensoid colloids on the basis of their behaviour to coagulation by electrolytes on dilution. In the discussions, they have tacitly assumed that the potential of the double layer on the particles remains constant on dilution though there is scarcely any recorded evidence in support of this assumption.

Attention may also be drawn to the discussions and controversies entered into by Weiser (*J. Phys. Chem.*, 1926, **30**, 20, 1527, also reference to earlier literature), Freundlich and Zeh, (*Zeit. physical Chem.*, 1924, **111**, 65) Dhar and Ghosh (*J. Phys. Chem.*, 1927, **31**, 649 ; *ibid.* **29**, 1925 ; p. 485,654 ; *Kolloid. Z.*, 1926, **38**, 141) on the influence of non-electrolytes on coagulation by electrolytes and on coagulation by mixtures of electrolytes. The necessity for simultaneous measurements of charges was pointed out by Mukherjee and and Ghosh (*J. Indian Chem. Soc.*, 1925, **1**, 213), and by Mukherjee, Chaudhury and Mukherjee (*J. Indian Chem., Soc.*, 1926, **3**, 849). In the present paper the following measurements of charges are recorded :

(*a*)   Variation in the charge on dilution of colloids with water; arsenious sulphide ; gold ; copper ferrocyanide.

[1](*b*)   Effect of ethyl alcohol on the charge of colloidal arsenious sulphide containing different concentrations of hydrochloric acid.

(*c*)   Effect of different concentrations of the following single electrolytes on the charge of particles of arsenious sulphide sol : hydrochloric acid, sodium, lithium and potassium chlorides, sodium benzoate, sodium citrate, potassium ferrocyanide.

(*d*)   Effect of the following mixtures of electrolytes on the charge of arsenious sulphide sol : sodium chloride and benzoate ; sodium chloride and oxalate ; sodium chloride and citrate ; barium chloride and sodium benzoate ; calcium and sodium benzoate, barium and sodium chlorides ; magnesium and sodium chlorides, lithium and magnesium chlorides, potassium ferrocyanide and chloride.

EXPERIMENTAL.

In these measurements the cataphoretic method developed by one of us (*Proc. Roy. Soc.*, *loc. cit.*) has been used. It is not possible to make measurements in this place during the rainy season on account of leakage. Attempts have been made to avoid it by insulating all connections and apparatus and by using paraffin oil instead of water in the thermostat. Though the trouble due to leakage can be sensib-

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[1] Measurements under this section have been exclusively carried out by Mr. S. G. Chaudhury.

ly diminished, it cannot be eliminated completely and the measurements have to be taken during the cold weather.

Two different glass tubes were used for cataphoresis. The effective distances were measured as usual from conductivity measurements.

One tube had four side tubes and the other two. The effective distance between the two side tubes enclosing the colloid-electlyte boundary were estimated to be 1·72 cm. and 4·2 cm. respectively for the upward movement of the colloidal particles (direct) and 1·78 cm. and 4·2 cm. respectively for the downward movement (reverse). *On using different tubes one finds some difference in the rate of migration per unit potential gradient.* This should be ascribed to the error in the determination of the effective distance*. The effective distance also varies with the specific conductivity of the electrolyte used for its determination. One gets a constant value and less variation in individual readings when the specific conductivity of the electrolyte is high —(greater than that of $N/200$ hydrochloric acid or $N/100$ copper sulphate). At low concentrations there is a discrepancy probably due to the fact that when the specific resistance is high the electrolyte in the immediate neighbourhood of the electrodes does not uniformly take part in the conduction—*i.e.*, the potential on account of the electrical field is not the same at all points in a a plane perpendicular to the axis of the tube. At higher concentrations due to the greater specific conductivity the zone of such irregular fields for the same potential gradient becomes smaller and smaller and the error in the determination of the effective distance becomes less than 1%. The figures for the rate of migration given in this paper (this holds true also for the data in the previous papers of Mukherjee and co-workers) therefore do not represent the absolute value. The cumulative effect of the errors in calculating the effective distance, and consequently the potential gradient, is not however great. So far using six different tubes we dave obtained a maximum variation of ±5% from these sources (*vide* Table I for illustration). *The rates of migration have been given in cms. per second per volt per cm. multiplied by* 10^s.

* Cf. *Proc. Roy. Soc., loc. cit.*, p. 112 : the following values for the unknown distance in cms. between the two lowest marks in each limb of the U-tube were obtained by placing the electrodes at different positions and using the same filling of electrolyte for measurements of conductivity : 17·18, 16·00, 18·22.

TABLE I.

Same Sample of Arsenious Sulphide Sol with two different Tubes.
Temp. 35°.

Tube.	Effective distance between the side limbs in cms.		Rate of migration.		
	Direct	Reverse	Direct	Reverse	Mean
I	1·72	1·78	50·83	51·4	51·115
II	4·2	4·2	47·29	48·7	48·08

Better agreement between individual measurements is observed when the boundary is in the same level in both the limbs which can be secured by initially using the requisite excess of the upper liquid in the bulb attached to the limb with the side tubes. Under the most satisfactory conditions, namely a sharp boundary and a fairly constant potential gradient the results are reproducible within 1·5% (*vide* Table II).

TABLE II.

Arsenious Sulphide Sol with a Mixture of ·00. N Barium Chloride and ·1134N Sodium Benzoate :   Temp. 35°.

Number of experiment.	Potential Gradient in volt per cm.		Rate of migration.
	Before	After	
1	·9788	·9968	40·6
2	·9787	1·009	40·2
3	·9647	·9960	40·8

The error is mostly due to that involved in reading the position of the boundary. It was found that the correction for the difference in viscosity is negligible when no non-electrolytes were used, in comparison to the error in reading the movement of the boundary. Even in the case of mixtures of electrolytes the variation in

viscosity was very small and varied from ·007288 for water (at 35°C) to ·007440. The rates of migration where corrected for viscosity differences have been given as ' corrected rate ' of migration in the following tables.

The methods of preparation of the colloids and other particulars are given in the following:

(a) Arsenious Sulphide Sol.

A saturated solution of arsenious oxide was mixed with twice its volume of conductivity water and the resulting solution was added to an equal volume of the water saturated with hydrogen sulphide which was then passed through the solution until all the arsenic had been transformed into arsenious sulphide. This took about one and half an hour. Then a current of hydrogen was passed till the sol was perfectly free from hydrogen sulphide. The sol was kept in Jena glass bottles wrapped up with black paper in a dark place but as care was not taken to have arsenious acid in excess the presence of polythionic ions cannot be denied (cf. Mukherjee and Chaudhury, loc. cit.). The sols contained about 16 millimoles of arsenious trisulphide per litre.

In order to secure a uniform electrolytic environment for the colloidal particles as shown by a constancy of the potential gradient before and after the migration, acid of slightly greater specific , conductivity in the ratio of 1·04 : 1 was used for the preparation of the upper liquid. The different samples of arsenious sulphide sol, prepared in the same way showed a considerable difference in the rate of migration per unit potential gradient as also a difference in electrical conductivity (cf. Mukherjee and Chaudhury, loc. cit.).

TABLE III.

Temp. 35°.

Sample No. ...	I	II	III	IV	V.	VI
Rate of migration ...	54·7	52·2	50·8	55 5	61·5	58·5

(b) Gold Sol.

The sol was prepared by Zsigmondy's nucleus method (Mukherjee and Papaconstantinou, J. Chem. Soc., 1920, 117, 1568).

On account of the difference in the density between the intermicellary fluid and the simple aqueous solution which was at first used as the upper liquid it is not possible to secure a stable boundary under such conditions as the colloid runs upwards in streaks. This difficulty however vanished on using the following procedure which also secured a liquid identical in ionic environment with the intermicellary liquid (as shown by the constancy of the potential gradient) and probably also identical with it in composition and density.

The original sol was at first precipitated with barium chloride solution and allowed to settle. The supernatant liquid was alkaline. Its pH was carefully determined from $E.M.F.$ measurements. A potassium hydroxide solution having the same pH was prepared in water and formaldehyde and ether were added to it in the same proportion as in the preparation of the sol. The solution was then boiled for a minute, $i.e.$, for the same time as in the preparation of the sol and cooled in a bath of cold water. A solution of potassium chloride of moderate concentration was prepared from portions of this liquid. The requisite quantity of the potassium chloride solution so prepared was added to another portion of the above liquid so that it had a specific conductivity greater than that of the sol in the ratio $1\cdot06:1$. The boundary was very sharp and stable and did not give any trouble. The sol had a tendency to settle. The rate of settling was recorded for sometime before and after the application of the electrical field. The rate of settling does not remain uniform. On keeping the tube undisturbed for 12 hours it is found that the boundary at first falls through a short distance and then remains steady. Also it appears that the rate of fall of the boundary after filling the tube depends on the rate at which the colloid level rises in the tube during the filling operation. These peculiarities are probably in part to be referred to local variations in viscosity and density. One might reasonably assume that these factors vary in such a manner during the direct and reverse movements that the mean of the two measurements will give the real rate of migration. Apart from any error inherent in the above assumption one has to remember that the conditions of an *electrically* stable boundary are not satisfied in the case of 'reverse' movements. But from numerous measurements on this and other sols it appears to us that *when the ionic environment is what we have been able to realise in these measurements the*

error involved in this uncertainty is not more than 3%, i.e., the mean may be taken to be correct within 1·5%. The actual data of the settling are also given in the tables dealing with this sol. It should be noted that even in the direct movement the settling was greater than the movement towards the anode for the potential gradients we have employed.

(c) *Copper Ferrocyanide Sol.*

Nearly equivalent quantities in solution of copper sulphate and potassium ferrocyanide crystals were mixed. The ferrocyanide solution was slightly in excess. The precipitate was filtered, carefully washed and transferred to a beaker. On keeping in contact with pure water overnight it peptised and was then dialysed for about a month and a half. It still contained a trace of ferrocyanide as is to be expected from the well known work of Duclaux.

As the upper liquid we used in this case, an equally conducting potassium chloride solution which gave satisfactory results in agreement with theoretical considerations.

RESULTS AND DISCUSSIONS.

In the following we have taken the mean of the direct and reverse movements to correctly represent the rate of migration. From the constancy of the potential gradient we consider that the electrical environment remains sufficiently uniform and constant during the migration and we think that we are justified in taking the mean of both movements as, the observed rate from the agreement between the two values. Besides the gravitational fall of the particles has always to be taken into consideration. For the arsenious sulphide sol the settling is small.

I.   *Effect of Dilution.*

Viscosity corrections were made for all the sols, taking the viscosity of water at the temperature to be unity. In the case of the gold sol only three measurements could be taken because of the low visibility of the boundary at higher dilutions. For the diluted sols the liquid used as upper liquid for the original sample was diluted correspondingly.

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TABLE IV.

Arsenious Sulphide

Viscosity of water=0·007283 (35°).

Dilution in ratio of volume of original sol to that of water added to it.	Relative viscosity.	Direct.	Reverse.	Mean corrected rate of migration.
pure sol	1·027	60·3	56·7	60·1
1:1	1·023	58·6	56·7	58·9
1:3	1·014	55·8	54·0	55·7
1:10	1·005	17·2	17·4	17·5
1:10	1·005	17·78*	17·2*	
1:20	·998	11·2	11·5	12·2
1:20	·998	12·7*	13·4*	

TABLE V.

Gold Sol. Temp. 35°.

Dilution.	Viscosity.	Time in minutes.	Settling of the boundary in centimeters.		Velocity.		Corrected rate of migration.
			Before.	After.	Direct.	Reverse.	
Pure sol	1·017	20	0·42	0·24	—10·0	41·1	15·8
1:1	1·011	15	0·75	0·25	—31·5	51·7	10·2
1:3	1·01	15	0·33	0·27	—27·6	38·6	5·6

TABLE VI.

Copper Ferrocyanide Sol. Temp. 35°.

Dilution.	Viscosity.	Direct.	Reverse.	Mean corrected rate of migration.
pure sol	1·415	52·2	47·6	70·6
1:1	1·1S	46·5	39·7	50·9
1:3	1·091	44·0	38·9	45·3
1:10	1·04	28·3	29·2	29·0

We observe in each case that the rate of migration per unit potential gradient as also the specific conductivity decreases on dilution. The present measurements have been carried out under more satisfactory and improved conditions than those obtaining in

Measurement taken after 3 days since mixing.

Mukherjee's earlier observations (*loc. cit.*) and there is not the same uncertainty of about 12% in our results. The decrease in the rate of migration of arsenious sulphide sols from CO to 12 leaves no doubt as to the effect of dilution. The arsenious sulphide sol seems to behave differently from the others in the initial stages of dilution where the rate varies very little at first for this sol, whereas there is a big drop in the other two cases. Assuming that the rate of migration represents the density of the charge we find that for arsenious sulphide sol the concentration of anions (to the primary adsorption of which the charge has to be ascribed) does not suffer marked diminution in the initial stages of dilution. The effect of the observed diminution in the charge will be to make the sol unstable on dilution against coagulation by electrolytes. Mukherjee and Sen (see also Kruyt and Spek) first pointed out that arsenious sulphide sols on dilution show a diminution in stability against precipitation by trivalent and an increase against univalent cations. They also found that depending on the extent of dilution the sol showed a diminution or increase in stability against (divalent) barium ion. Burton and Bishop (*J. Phys. Chem.*, 1920, **24**, 701) who later generally confirmed the above observations, tried to classify the electrolytes on the basis of the valency of the cations. This is evidently erroneous as appears from the behaviour of the sol against precipitation by barium ions. The diminution in stability observed against trivalent cations has been explained by Mukherjee and Kruyt on the ground that on dilution the colloid-liquid interface also diminishes. The decrease in the charge on dilution we have observed would diminish the stability and the increase in distance on dilution would act oppositely. But these factors would act in the same manner for different electrolytes. The explanation of the behaviour of the sol in the presence of trivalent cations referred to above thus remains valid. It has been argued by Weiser and Dhar that the adsorption of both chloride and potassium ions is considerable and that on dilution the ratio of the adsorption of chlorine to potassium ions becomes greater so that the negative charge of the particles is greater for a diluted sol. Ghosh and Dhar (*J. Phys. Chem.*, 1927, **31**, 193) in fact, have analytically measured the simultaneous adsorption of copper and chlorine ions in the case of positively charged manganese dioxide sol and found that "the ratio of the amount of adsorption of cupric ion to that of chlorine ion is greater" with a diluted sol than the concentrated one. On account

of analytical difficulties, we think that this indirect evidence is not satisfactory and that direct measurements of the charge are necessary. Such measurements are in progress.

II. *Effect of Non-electrolytes on the Charge of Arsenious Sulphide Sol* (S. G. C.)

Preliminary measurements have been taken with ethyl alcohol, methyl alcohol and *iso*-amyl alcohol. The upper liquid taken, was hydrochloric acid of slightly greater conductivity than that of the colloid with the same percentage of alcohol. Under these conditions the potential gradient before and after the movement of the boundary remained constant and the colloid-liquid boundary was very sharp. In considering the effect of the addition of non-electrolytes, the consequent variation in the osmotic and activity co-efficients of the electrolytes have to be taken into consideration. Besides it has to be remembered that the initial rate of migration on the addition of the non-electrolytes and in the absence of electrolytes is different. Further in interpreting the influence of non-electrolytes, the effect of the change in the di-electric constant both in the bulk and in the double layer (the two are perhaps not the same; *cf* Born, *Z. Physik*, 1920, 1, 45, 221; Debeye and Macaulay, *Annual Reports, Chem. Soc., London*, 1925, p. 85; 1926, p. 128) have to be taken into consideration. We give below some observations which go to show that ethyl alcohol diminishes the rate of migration. Because of the theoretical interest of such measurements a detailed investigation is in progress.

TABLE VII.

Concentration of hydrochloric acid = 0·0158N.

Ethyl alcohol	Corrected rate of migration
0	43·5
2½	38·7
5	85

TABLE VIII.

Concentration of hydrochloric acid = 0·0079 N.

% of Ethyl alcohol (by volume)	Corrected rate of migration
0	47·3
2½	46·5
5	41·4
10	40·2

III. *Variation of the Charge of Arsenious Sulphide Sol with Concentrations of single Electrolytes* :

TABLE IX*

Hydrocholric acid. Temp. 35°.

Concentration of electrolyte	Rate of migration		
	Direct	Reverse	Mean
0	54·5	49·5	52·0
·001 N	50·9	45·2	48·1
·002 N	40·9	45·9	43·4
·004 N	38·7	44·5	41·6
·01 N	39·4	42·8	40 6

TABLE X

Potassium Chloride. Temp. 85°.

Electrolyte concentration.	Rate of migration		
	Direct	Reverse	Mean
0	54·7	56	55·4
·000025 N	55·6	51·5 (?)	58·6
·00005 N	50·2	52·8	51·5
·0001 N	49·3	51·7	50·5
·0002 N	44·2	45·1	44·6
·001 N	40·6	43·9 (?)	42·3
·002 N	38·6	40·6	39·6
·01 N	36·6	37·2	36·9
·02 N	33·1	35·4	34·3

* The measurements with hydrochloric acid were not as satisfactory as could be realised. This is evident from the greater difference between the direct and reverse movements.

TABLE XI.

Sodium Benzoate. Temp. 35°.

Electrolyte concentration	Rate of migration		
	Direct	Reverse	Mean
0	52·2	54·0	53·1
·00005 N	54·2	53·1	53·7
·0001 N	57·1	54·6	55·9
·001 N	50·0	49·5	49·8
·002 N	48·7	48·1	48·4
·005 N	45·8	46·2	46·0
·005 N	47·2	47·4	47·3
·01 N	47·6	48·5	48·1
·01 N	46·9	48·8	47·9
·04 N	46·2	47·8	47·0
·1 N	41·4	42·6	42·0

TABLE XII.

Sodium Citrate.   *Temp. 35°.*

Electrolyte concentration	Rate of migration		
	Direct	Reverse	Mean
0	47·30	48·7	48
†·00005 N	46·1	46·5	46·3
·0001 N	49·2	48·4	48·8
·002 N	49·7	50·7	50·2
·01 N	51·8	50·6	51·2
·1 N	46·6	49	47·8

† This initial decrease has been confirmed with another sol.

TABLE XIII.

Potassium Ferrocyanide. Temp. 35°.

Electrolyte concentration	Rate of migration		
	Direct	Reverse	Mean
0	61·5	57·9	59·7
·004 N	57·5	55·9	56·7
·01 N	66·2	66·3	66·2
·03 N	66·8	63·2	65

We find that in the case of hydrochloric acid and potassium chloride[1] there is a decrease in the charge at all concentrations. Sodium benzoate shows two maxima followed by the usual decrease. Sodium citrate shows an initial decrease followed by an increase. The charge again diminishes. Potassium ferrocyanide shows an initial decrease and then an increase which persists upto the highest concentrations recorded. The initial variations with these three electrolytes are complex probably because of interactions between the anions in the surface and those in the added electrolyte including hydroxyl ions which are likely to be present as a result of hydrolysis at least in the case of the benzoate and the citrate (cf. Mukherjee and Chaudhury, *loc. cit.*). Sodium citrate and potassium ferrocyanide show a higher charge than that of the pure sol upto a concentration of 0·01 N and 0·03 N respectively. Considering the effect of these electrolytes on the charge alone and comparing equivalent concentrations we find that potassium ferrocyanide ought to have the greatest stabilising effect, sodium benzoate coming next after it followed by sodium citrate. The chloride ion is comparatively weakly adsorbed.

We would refer here to the following earlier measurements with sodium and lithium chlorides which show that there is actually an increase in the negative charge at low concentration in the case of lithium and sodium chlorides and that the initial increase is

[1] The measurements for the concentrations ·000025 N and ·001 N in the case of potassium chloride show a greater divergence between the direct and reverse movements than in the case of the others.

greater for lithium than for sodium ; whereas we have just observed that potassium chloride and hydrochloric acid show a diminution at all the concentrations studied.

TABLE XIV.

Sodium Chloride.

Conc. of the electrolyte	Rate of migration
0	51
·00006 N	57·8
·0001 N	54·2
·0002 N	48·7
·001 N	45·4
·02 N	39·8

TABLE XV.

Lithium Chloride.

Conc. of the electrolyte.	Rate of migration
0	51
·00005 N	59·7
·0001 N	55·1
·0005 N	47
·005 N	48·5

Regarding the interpretation of this rise in the rate we would refer to the considerations set forth by Mukherjee and Iyer (*J. Ind.*

Indian Chem. Sec., 1926, **3**, 307,) which show that the initial rise is to be ascribed to the adsorption of chlorine ions.

IV.   Variation of Charge with Mixtures of Electrolytes.

TABLE XVI.

Sodium chloride and sodium benzoate   Temp. 35°

Conc. of sodium chloride.	Conc. of sodium benzoate	Rate of migration.		
		Direct.	Reverse	Mean.
0	0	54·7	56	55·4
·005 N	0	43·5	43·3	43·4
,,	·001 N	46·7	46·2	46·5
,,	·002 N	44·4	45·4	44·9
,,	·005 N	37·6	37·7	37·7
,,	·01 N	33	33·9	33·5

TABLE XVII.

Sodium chloride and sodium Oxalate   Temp. 35°.

Conc. of sodium chloride.	Conc. of sodium oxalate.	Rate of migration.		
		Direct.	Reverse.	Mean.
0	0	54·7	56	55·4
·005 N	0	43·5	43·3	43·4
,,	·001 N	46·2	48·3	47·3
,,	·002 N	44·9	45·8	45·4
,,	·005 N	43	45	44
,,	·01 N	40·5	42·6	41·6

TABLE XVIII.

Sodium chloride and sodium citrate   Temp. 85°.

Conc. of sodium chloride.	Conc. of sodium citrate.	Rate of migration.		
		Direct.	Reverse.	Mean.
0	0	54·7	56	55·4
·005 N	0	43·5	43·8	48·4
,,	·001 N	43·8	43·1	43·5
,,	·002 N	47 8	48·6	48·2
,,	·005 N	44·9	43·8	44 4
,,	·01 N	36·2	37·6	86·9

TABLE XIX.

Barium Chloride and Sodium Benzoate.   Temp. 85°.

Conc. of barium chloride.	Conc. of sodium benzoate.	Rate of migration.		
		Direct.	Reverse.	Mean.
0	0	55·5	51·5	53·5
·001 N	0	20·7	19·7	20·2
,,	·034 N	40·9	40·7	40·8
,,	·0567 N	45·3	45·4	45·4
,,	·085 N	45	43·4	44·2
,,	·1134 N	40·8*	41·2*	41
,,	,,	40·6*	(?) 38·1*	36·9
,,	,,	40·2*	40·2*	40·2

TABLE XX.

Calcium Benzoate and Sodium Benzoate. Temp. 35°.

Conc. of calcium benzoate	Conc. of sodium benzoate.	Rate of migration.		
		Direct.	Reverse.	Mean.
0	0	55·5	51·5	53·5
·0015 N	0	9·6	8·5	9·1
,,	·084 N	38·6	28·9	38·7
,,	·0567 N	47·4	46	46·7
,,	·085 N	44·8	45·9	45·4
,,	·1134 N	35·9*	37·4*	35·3

TABLE XXI.

Barium chloride and sodium chloride. Temp. 35°.

Conc. of barium chloride.	Conc. of Sodium chloride.	Rate of migration.		
		Direct.	Reverse.	Mean.
0	0	55·5	51 5	53·5
·001 N.	0	20·7	19·7	20·2
,,	·015 N	36·8	37·7	37·3
,,	·025 N	40·9	35·6	40·3
,,	·0375 N	38·4	40·9	39·7
,,	·05 N	The sol coagulated on admixture.		

* In these cases a curious effect was observed. Although the charge was much greater than that for the single electrolyte, an appreciable amount of the sol coagulated in the tube while measurement was being taken.

TABLE XXII.

Magnesium chloride and sodium chloride.   Temp.   35°.

Conc. of magnesium chloride.	Conc. of sodium chloride.	Rate of migration.		
		D rect.	Reverse.	Mean.
0	0	61·5	57·9	59·7
·0015 N	0	15	16	15·5
,,	·015 N	32·4	33·9	33·2
.,	·025 N	42·4	42·4	42·4
,.	·0375 N	43·1	42	42·6
,,	·05 N	The sol coagulated on admixture.		

TABLE XXIII.

Magnesium chloride and Lithium chloride.   Temp. 35°

Cong. of magnesium chloride.	Conc of lithium chloride.	Rate of migration.		
		Direct.	Reverse.	Mean.
0	0	61·5	57·9	59·7
·0015 N	0	15	16	15·5
,.	·016 N	24·9	27·2	26·1
,,	·027 N	46·9	45·2	46·1
,,	·04 N	51·5	·49·2	50·4

Concentration of electrolytes: 1 div. = ·01 moles.
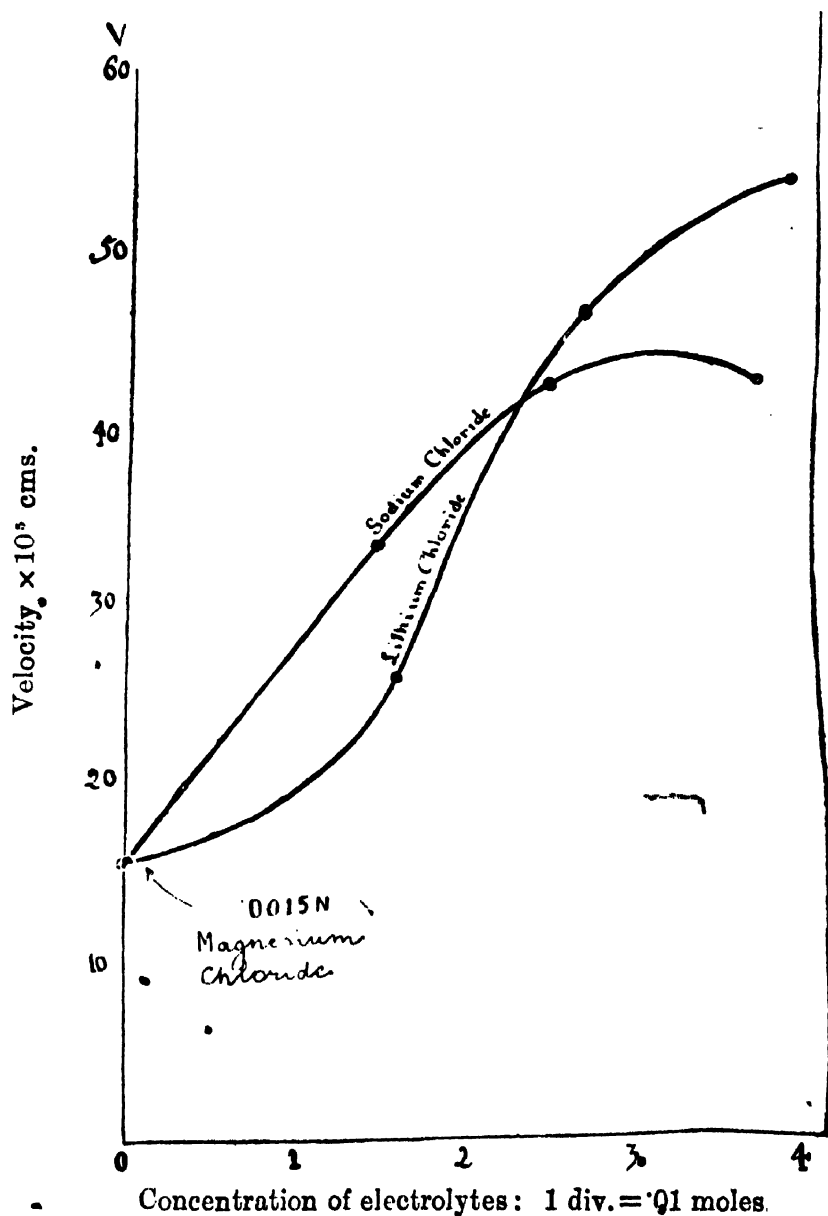
TABLE XXIV.

Potassium chloride and Potassium ferrocyanide. Temp. 35°.

Conc. of potassium chloride.	Conc. of potassium ferrocyanide.	Rate of migration.		Mean.
		Direct.	Reverse.	
0	0	61·5	57·9	59·7
·004 N	0	50·3	50·1	50·2
,,	·004 N	60·6	59	59·8
,,	·01 N	49	49·3	49·2
,,	·03 N	The sol coagulated.		

Attention has of late been directed to the problem of finding an explanation for the so-called ionic antagonism which plays an important part in the biological sciences (*cf.* Freundlich and Scholz, *Koll. Beih.*, (1922), **14**, 267 ; Mukherjee and Ghosh, *loc. cit.*)., Investigations dealing with the general aspects of the problem of coagulation of colloids by mixtures of electrolytes have been also carried out by Weiser (*J. Phys. Chem.*, (1921), **25**, 665, **28**, 232, (1924), (1926) **30**, 20. and (1926) **30**, 1527), Ghosh and Dhar (*J. Phys. Chem.*, (1925) **29**, 435 and 659), and Sen (*s. anorg. Chem.*, 1925, 149, 130; *J. Phys. Chem.*, (1925) **29**, 517. and by Kruyt and Willigen (*K. Akad. Wentensch, Amsterdam*, (1926) **29**, 484).

The experimental work on this subject has centred round measurements of coagulating values and some limited measurements of adsorption of the ions of the electrolytes, mostly carried out by Weiser. The absence of measurements of charges has already been commented upon. Mukherjee and Ghosh (*loc. cit*). first worked with mixtures of electrolytes having a common cation and concluded (p. 220) " that even in cases where the displacement of adsorption of one cation by another is not possible the effect of the anion is as pronounced as in the case where displacement of

adsorption may occur in addition." They also state (p. 228) "the initial rise in charge at low electrolyte concentrations is to a large extent responsible for all these effects."

From the data given above we find that there is evidence of an initial increase in the charge on the addition of citrate, benzoate and ferrocyanide. In each of the Tables from XVI to XXIV the charge of the colloidal particles under the following conditions have been given :

(a) without any electrolyte, (b) with only the electrolyte whose concentration remains fixed, and (c) with different concentrations of the second electrolyte.

A comparison of the charges under conditions (a), (b) and (c) just mentioned *shows that there is a rise in the charge when the concentration of the second electrolyte is small.* When the two electrolytes have a cation in common, there is no question of a displacement of adsorption of one cation by another. In the case of benzoate (Table XI) the increase in the charge leaves no doubt as to its greater adsorption than that of the chloride ion. In the case of the oxalate (Table XVII) and the citrate (Table XII) though there is no doubt that some of the anions originally present in the primary layer are displaced by them, the rise as such constitutes no evidence as to their greater adsorbability than say the chloride ion ,for a slight displacement will increase the negative charge because of their greater valencies. Some displacement can be expected even if their adsorbability is smaller. In Tables XIX to XXIII the electrolyte with a fixed concentration contains a cation of higher valency. In Table XIX there are two cations and two anions and in Tables XX to XXIII we have a common anion. *The displacement of the adsorption of a divalent cation (barium or calcium) in the fixed sheet of the double layer by sodium ions is definitely proved from the data recorded in the three Tables XX to XXII and we are dealing with an interchange of ions in the double layer of the type referred to by* Mukherjee and Iyer (*loc. cit*). That magnesium is more weakly adsorbed than barium is evident from their respective effect on sodium chloride.

From Tables XXII and XIII (see also Fig. 1) we find that at low concentrations lithium has a smaller effect on the displacement of the adsorption of magnesium ions than sodium has in keeping with its lower adsorbability. In discussing these cases of displacement of adsorption on the basis of the variation in the charge we have to

remember that besides the relative adsorbability we have to consider the valencies. Considering the portion of the lithium chloride curve below that of sodium chloride we see that though the displacement of the adsorption of magnesium chloride by lithium is less, as the concentration of the lithium coloride rises, the displacement increases and on account of the weaker adsorbability of the lithium ions, which begins to be felt more and more strongly from about a concentration of ·016 N., the negative charge rises abruptly until it passes over the curve of sodium chloride. At higher concentrations the relatively greater adsorbability of sodium ions lowers the negative charge to a greater extent.

In Table XXIV we have a common cation and two different anions. The increase in the charge on the addition of potassium ferrocyanide shows clearly the primary adsorption of the ferrocyanide ions. It does not mean however that the adsorption of ferrocyanide ion is considerably stronger than that of chloride ion as there is a difference in valency. The adsorption of the ferrocyanide ·ion would seem to be stronger than what appears to be the case from the above data if the concentrations are expressed in terms of gram ions and not in terms of gram equivalents.

From the above we see that both the displacement of the cation and the adsoiption of the anion have to be considered in explaining the coagulation of colloids by mixtures of electrolytes. Also that both these factors affect the coagulating concentration of the second electrolyte through an increase in the negative charge of the primary layer.

V. *Relation between Charge and Coagulating Concentration.*

Regarding however the relationships between the charge and the coagulating concentrations we find that these are not simple. We would like to point out that in many cases it was noted that the sol to which two electrolytes have been added coagulated although the charge of the particle was much higher than in the absence of the second electrolyte (*vide* Tables XXI and XXII, c.p. also XX). Obviously the stability is not so directly related to the charge as is generally believed to be the case. Thus the electrolytes with divalent cations depress the charge enormously. We have stable sols with these electrolytes where the particles show a rate of migration

ranging from 20 to as far as low as 9 (calcium benzoate). From the slope of the curve with potassium, sodium or lithium chloride as the added electrolyte it would appear that coagulation takes place before a velocity of about 20 has been reached. We would particularly refer to the low charge with calcium benzoate.

PHYSICAL CHEMISTRY LABORATORY,
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CALCUTTA.

ERRATA

For	Read	Page	Line
Only 6 g. ...	Only $0 \cdot 6$ g.m. ...	431	15
Manganese Dioxide on Nickel Hydroxide.	Manganese Hydroxide on Nickel Hydroxide.	432	15
Rare earth ...	Rare earth oxide ...	435	10
2 small pieces ...	Small pieces ...	435	28
Rose from ...	Rose slowly from ...	436	19
$PtCl_{11} . 2 Et_2$. ...	$PtCl_2, 2 Et_2$. ...	468	2
$PtCl_2, 3 C_2H_4 (pH_2)_2$	$2 PtCl_2 . 3 C_2H_4 (NH_2)_2$ ...	468	25 •
Ag Cl NH ...	Ag $ClNH_3$ ...	468	30

The Cyclic Processes involved in the Manufacture of Sodium Nitrate from Chilean Caliche.

By Mohammed Abdul Hamid.

Sodium nitrate occurs in large quantities in South America and is generally known as Chile Saltpetre. The crude material from which the Chile saltpetre is manufactured is commonly called *caliche*.

The main constituents of the water soluble products of most of the nitrate deposits of Chile are the nitrates, sulphates and chlorides of sodium and in smaller quantities those of calcium, magnesium and potassium. To these may be added the chlorates, borates and iodates and salts of aluminium, iron and chromium, which occur in very small quantities.

The raw material is usually crushed to small pieces and then leached with water according to various modifications of the Shank's process. The *Aqua Vieja* or the cold extract is then taken to the boiling tanks where the necessary amount of evaporation is carried out. The *caldo* or the hot liquor then goes to the crystallising vats where it is allowed to cool and the crystallised salts removed by filtration. The mother-liquor, after the addition of the requisite amount of water to it is used again for the leaching operations.

As mentioned above the main constituents of the water-soluble products of most of the caliches are the sulphates, nitrates and chlorides of sodium. The solubility of sodium chloride in nitrate liquors is not much affected by change in temperature and since it occurs as a solid saturant at all stages, its presence may be disregarded. The system, $H_2O - Na_2SO_4 - NaNO_3$ at 25° has been recently investigated by the author (*J. Chem. Soc.*, 1926, 129 203). The addition of sodium chloride to this system will cause a slight change in the solubilities of the two salts but will not affect the nature of this system since sodium chloride is not known to form any compounds with either sodium sulphate or sodium nitrate. We shall therefore suppose that the relations in this system at 25° are those shown in Fig. I even in the presence of excess of sodium chloride. This figure is taken from the paper above mentioned.

It will be seen by reference to Fig. I, that the system H_2O- $Na_2SO_4-NaNO_3$ at 25° is complicated by the existence of a hydrated double salt which is composed of one molecule of sodium sulphate, one molecule of sodium nitrate and one molecule of water. The composition of this compound is represented by the point D in weight percentages in Fig. I. The following points may carefully be noted in this figure :—

(*i*) Points in the area cAD represent complexes of the solution c and of the two solids sodium sulphate and the compound D in varying proportions.

(*ii*) Points in the area dDB represent complexes of the solution d with mixtures of sodium nitrate and the compound D of varying proportions.

(*iii*) Points in the area DAB represent dry mixtures of sodium nitrate, sodium sulphate and the compound D. No solution can exist here because there is not enough water to combine with sodium sulphate and sodium nitrate to form the compound D.

In order that the phenomena which occur during the leaching of caliche may be properly understood, we shall study the behaviour of dry mixtures of sodium nitrate and sodium sulphate of varying compositions on the gradual and isothermal addition of water at 25°. Suppose n_1 and n_2 represent the number of mols. of sodium nitrate and sodium sulphate in a given nitrate-sulphate mixture. Three cases may be distinguished. When,

$$(i) \quad \frac{n_1}{n_2}=1 \quad \text{or} \quad n_1=n_2$$

$$(ii) \quad \frac{n_1}{n_2}< 1 \quad \text{or} \quad n_2> n_1$$

$$(iii) \quad \frac{n_1}{n_2}> 1 \quad \text{or} \quad n_1 > n_2$$

or expressed in proportions by weight, when,

$$(i) \quad \frac{w_1}{w_2} =\frac{85}{142} \quad \text{or} \quad w_1={\cdot}6w_2$$

$$(ii) \quad \frac{w_1}{w_2} <\frac{85}{142} \quad \text{or} \quad w_1<{\cdot}6w_2$$

$$(iii) \quad \frac{w_1}{w_2} >\frac{85}{142} \quad \text{or} \quad w_1 >{\cdot}6w_2$$
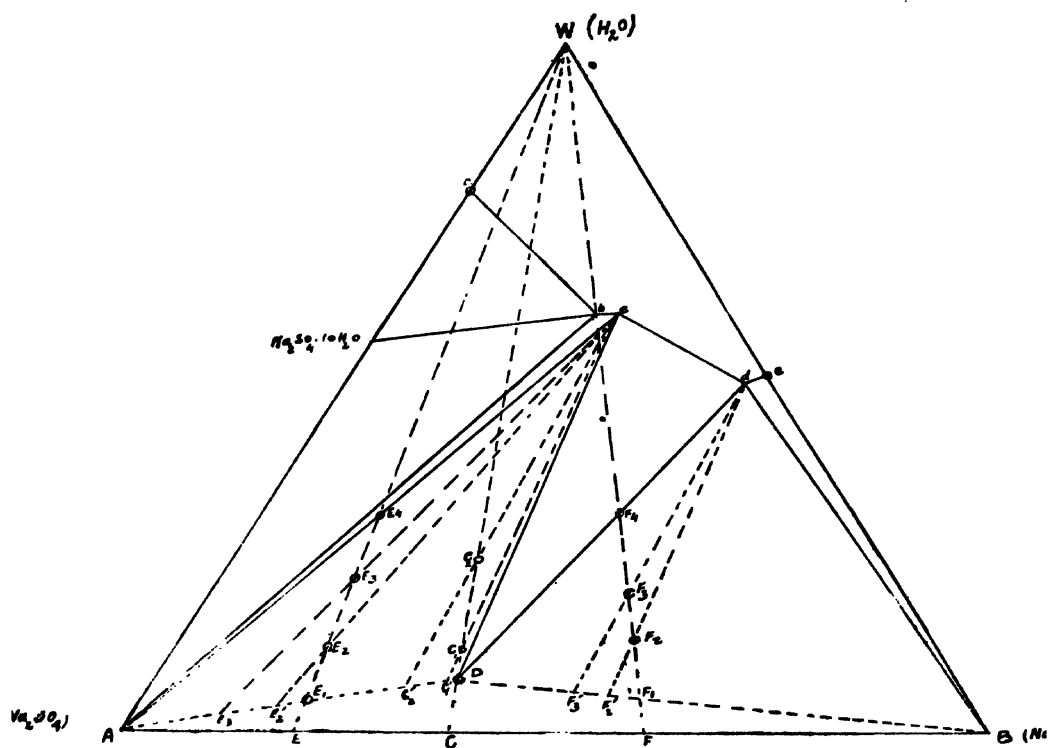
FIG. 1
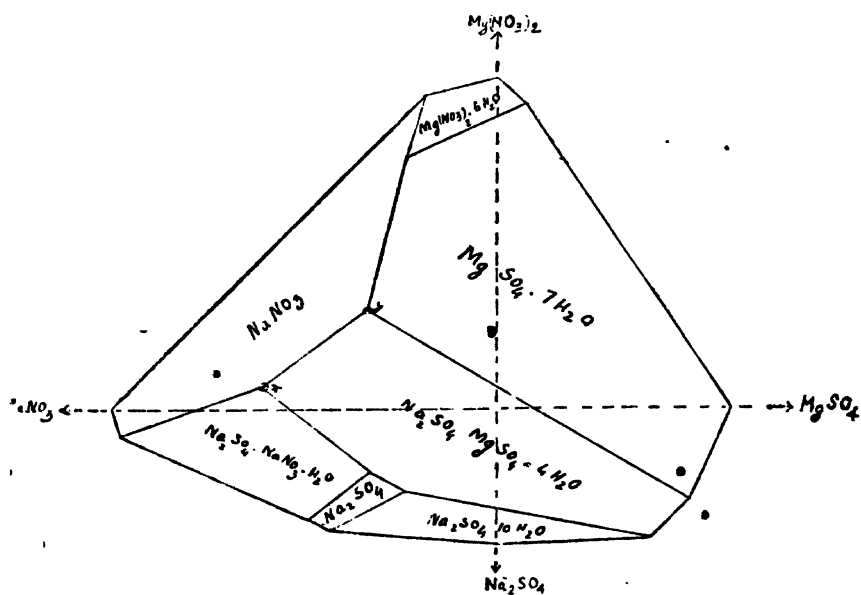
FIG. 2

Case I. When $n_1 = n_2$ *i.e.*, when the mixture contains equal number of mols. of sodium sulphate and sodium nitrate. It is clear that when a certain amount (n mols.) of water is added to such a mixture, the whole of sodium nitrate will combine with the whole of sodium sulphate to form the hydrated sulphate-nitrate compound D. We shall see the various changes which take place on the gradual and isothermal addition of water to such a mixture at 25°. Expressed in weight percentages,

$$w_1 + w_2 = 100$$

$$w_1 = \cdot 6w$$

∴ $w_1 = 37\cdot5$ and $w_2 = 62\cdot5$ *i.e.*, the mixture contains 37·5 parts by weight of sodium nitrate and 62·5 parts by weight of sodium sulphate. The composition of this mixture is represented by the point C in Fig. I. On the gradual and isothermal addition of water to this mixture at 25°, the composition of the complex so formed would change along the line CW in the direction CW. It may be seen that the point D which represents the composition of the nitrate-sulphate compound lies on the line CW, *i.e.*, it contains sodium sulphate and sodium nitrate in the same proportions as is contained by the dry mixture C. Suppose so much of the water is added to the mixture C that the composition of the complex is represented by a point on the line CW between the points C and D. Since this point lies in the area DAB, it is impossible for any solution to exist (see above) and the complex will therefore consist only of dry mixtures of sodium sulphate, sodium nitrate and the compound D. When so much of the water has been added to the mixture C that the composition of the complex is represented by the point D, the whole of sodium nitrate combines with the whole of sodium sulphate and the whole of water added to form a homogeneous solid phase of the composition D, *i.e.*, the nitrate-sulphate compound. From this point onward therefore we may regard further dilution as the dissolution of the compound D in water. This dissolution is not normal, since water causes the dissociation of a portion of the solid D into its respective components and the solid in contact with solution is of a heterogeneous character consisting of a mixture of the compound D and one of its dissociation products, sodium sulphate. Suppose the composition of the complex at any one time is represented by the point C_1. This point represents a complex of the solution c and of a mixture of solid D and solid sodium sulphate.

in the proportion of,

$\dfrac{C_1 C'_1}{cC'_1}$ parts of the solution c and $\dfrac{cC^1}{cC'_1}$ parts of $D + Na_2SO_4$.

The proportion of D and Na_2SO_4 in the solid mixture is given by the ratio in which the line cC_1 when produced divides the line DA, i.e.,

$\dfrac{AC'_1}{AD}$ parts of D and $\dfrac{C'_1 D}{AD}$ parts of Na_2SO_4.

In order to keep the composition of the solution c constant, more of the compound D dissociates on increasing additions of water. Thus when the composition of the complex is represented by the point C_2 the proportions of the compound D and of sodium sulphate in the solid mixture are,

$\dfrac{C'_1 D}{AD}$ parts of Na_2SO_4 and $\dfrac{AC'_1}{AD}$ parts of D.

It may be observed here that the whole of the sodium nitrate which is produced by the dissociation of the compound D is dissolved while the solution dissolves only a portion of the sodium sulphate which is thus produced, the rest being precipitated as such in the solid form. Therefore on the addition of increasing amounts of water, the proportion of sodium sulphate in the solid phase goes on increasing while that of the compound D goes on decreasing and the solution in all these changes retains the constant composition c. When so much of the water has been added that it effects the complete dissociation of the compound D, this compound disappears as a solid phase. On further additions of water therefore, the composition of the solution changes along the curve cb in the direction cb i.e., in a direction in which the solution contains diminishing quantities of sodium nitrate. We are not concerned here with these changes. Our only object has been to show that on the isothermal addition of water at 25° to a dry sulphate-nitrate mixture which contains equal number of molecules of sodium sulphate and sodium nitrate, the strongest solution that can be obtained with respect to sodium nitrate concentration is of the composition c.

Case II. When $n_2 > n_1$ i.e., when the number of molecules of sodium sulphate exceeds the number of molecules of sodium nitrate

in the dry mixture or expressed in proportions by weight when the weight of sodium nitrate is less than three-fifth of the weight of sodium sulphate in the dry mixture. The composition of one such mixture is given by the point E in Fig. I in weight percentages. When so much of the water is added to the mixture E that the composition of the dry mixture is represented by the point E_1, the whole of the sodium nitrate present combines with the whole of water added and three-fifth parts by weight of the whole of sodium sulphate present to form the compound D and the excess of sodium sulphate remains as such in the solid form. E_1 is therefore a dry mixture of

$$\frac{AE_1}{AD} \text{ parts of } D \text{ and } \frac{E_1 D}{AD} \text{ parts of } Na_2SO_4.$$

The various changes that occur on the gradual addition of water at 25° to this mixture along the line EW in the direction EW can be deduced in the same manner as in the first case by reference to Fig. I. It will be seen here that as in the former case the composition of the strongest solution with respect to sodium nitrate concentration which can be obtained from a dry mixture in which the molar ratio of sodium nitrate to sodium sulphate is less than one is given by the point c in Fig. I.

Case III. When $n_1 > n_2$ *i.e.*, when the number of molecules of sodium nitrate exceeds the number of molecules of sodium sulphate in the dry mixture. Suppose

$$n_1 = n_2 + x.$$

When n_2 mols. of water are added to this mixture they will combine with n_2 mols. of sodium nitrate and the whole of sodium sulphate to form n_2 mols. of the compound D and the solid mixture will at this stage contain n_2 mols. of D and x mols of free solid sodium nitrate. These relations may be expressed in weight percentages as follows :—

$$w_1 + w_2 = 100$$

Suppose $\quad w_1 = {\cdot}6w_2 + x_1$

and $\quad w_2 = 40$

then $\quad x_1 = w_1 - {\cdot}6w_2 = 86$

i.e., in a mixture which contains 40 parts by weight of sodium sulphate and 60 parts by weight of sodium nitrate, only 36 parts by weight of sodium nitrate will be free to dissolve as such and the remaining 24 parts by weight of sodium nitrate will combine with 40 parts by weight of sodium sulphate to form the compound D when water interaction takes place. The same thing can be shown by reference to Fig. I. The composition of a mixture which contains 40 parts by weight of sodium sulphate and 60 parts by weight of sodium nitrate is given by the point F in Fig. I. The composition of the mixture F can be represented either by reference to the line AB or to the line CB. Referring it to the line CB we have the composition of F in weight percentages,

$$F = \frac{100CF}{CB} \text{ parts of } B \text{ and } \frac{100FB}{CB} \text{ parts of } C.$$

We have seen in Case I that when $AB=100$, $CB=62\cdot5$, so that

$$CF=CB-FB=62\cdot5-40 = 22\cdot5.$$

$$\therefore F= \frac{100\times22\cdot5}{62\cdot5} \text{ parts of } B \text{ and } \frac{100\times40}{62\cdot5} \text{ parts of } C.$$

i.e., 36 parts by weight of B or sodium nitrate and 64 parts by weight of C.

We started with a mixture of 60 parts by weight of sodium nitrate and 40 parts by weight of sodium sulphate. Out of 60 parts, sodium nitrate is distributed as 36 parts in the phase B or is present as such and $(60-36)$ or 24 parts in the mixture C which also contains all the 40 parts of sodium sulphate present in the original mixture. It may be pointed out that this is only an imaginary distribution. The actual distribution of sodium nitrate only takes place in the presence of water.

On the addition of water at 25° to the mixture F, the composition of the mixture changes along the line FW in the direction FW. Between the points F and F_1 it is not possible for any solution to exist and points on the line F_1F between the points F and F_1 represent compositions of dry mixtures of C, the compound D and the phase B or free sodium nitrate, in other words on account of insufficient quantity of water, only a part of the mixture C is converted into the compound D. When so much water has been added that

the composition of the mixture is represented by the point F_1 the whole of the mixture C is converted into the compound D and the point F_1 represents a mixture of the compound D and the phase B or free sodium nitrate in the proportion of

$\dfrac{DF_1}{DB}$ parts of B or free sodium nitrate and $\dfrac{F_1B}{DB}$ parts of the compound D. On the addition of increasing quantities of water, the mixture F yields complexes of the solution d with mixtures of solid sodium nitrate and the compound D in varying proportions. When the composition of the complex is represented by the point F_2 it contains

$\dfrac{F_2F'_2}{F'_2d}$ parts of the solution d and $\dfrac{F_2d}{F'_2d}$ parts of the mixture F'_2

which contains

$\dfrac{DF'_2}{DB}$ parts of solid sodium nitrate and $\dfrac{F'_2B}{DB}$ parts of the compound D. On further additions of water when the composition of the complex is represented by the point F_3, the solution d is in contact with a mixture which contains,

$\dfrac{DF'_3}{DB}$ parts of solid sodium nitrate and $\dfrac{F'_3B}{DB}$ parts of the solid compound D. It is clear therefore that on increasing additions of water the proportion of free sodium nitrate decreases and that of the compound D increases in the solid mixture while the solution retains the constant composition d. When so much of the water has been added that the composition of the complex is represented by the point F_4, sodium nitrate disappears as a solid phase and the solution d is in contact with the solid compound D only. If at this stage the solution d is separated from the solid compound D by filtration, we have,

$\dfrac{DF_4}{Dd}$ parts of the solution d, and $\dfrac{F_4d}{Dd}$ parts of the compound D.

If this solid compound D is dissolved separately in water, we have shown in Case I that the composition of the strongest solution with respect to sodium nitrate concentration which can be obtained from it is that represented by the point c. To sum up we can say that on the isothermal addition of water to a dry mixture of sodium nitrate and sodium sulphate in which the number of molecules of

sodium nitrate exceeds the number of molecules of sodium sulphate by x, we can get an amount of the solution d corresponding to x only i.e., to the free nitrate only and an additional solution of the remaining (combined) nitrate at a maximum concentration of sodium nitrate equal to that contained by the solution c.

Very recently a process has been invented by Guggenheim brothers in America, who claim that 'their invention will make possible a leaching process operating in such a manner as to permit a cold or tepid leaching of caliche in a cyclical and orderly manner, which will accomplish substantial dissolution of all the sodium nitrate in normal caliches and will permit the production of the entire solution as strong solution approaching or exceeding the solubility of free nitrate at 25°, in contradistinction to the production of a portion of the solution at a maximum concentration of the nitrate equal to that contained by the solution c, the production of which is maintained by the authorities in the industry to-day as necessary to obtain commercially satisfactory extraction.' They state that an efficient and desirable way of preventing the disturbing influence of the nitrate-sulphate compound is by controlling and properly proportioning the content in the caliches and in the leaching solutions of the salts of magnesium, calcium and potassium, which have in the past practice of the industry been considered unimportant constituents, and to the presence of which no significance in this connection was attached. These salts can be characterised as those which are able to exert preferential combining affinities for the sulphate radicle group (SO_4) or for sodium sulphate. The chief of these are salts of calcium, potassium and magnesium. Stripped of the garb of technicalities, the Guggenheim process can be easily explained by the following example :—

Although the quaternary system, $H_2O-Na_2SO_4-NaNO_3-MgSO_4-Mg(NO_3)_2$ at 25° has not been worked out or at least the results have never been published, it is probable that the relations in this system will not be very different from those shown in Fig. II. Jackman and Brown (J. Chem. Soc., 1922, 121, 691) have shown that the only solid phases in the system, $H_2O-MgSO_4-Mg(NO_3)_2$ at 25° are $MgSO_4.7H_2O$ and $Mg(NO_3)_2.6H_2O$, but it is very likely that the hexa-hydrate of magnesium sulphate ($MgSO_4.6H_2O$) and even Kieserite ($MgSO.H_2O$) may appear as solid phases at 25° in the above quaternary system. Since it is immaterial for the present purpose whether the lower hydrates of magnesium sulphate appear

in the quaternary system or not, they are not shown in Fig. II. From this figure it will be seen that all along the curve xy between the points x and y, the quaternary solutions are in equilibrium with two solids, sodium nitrate in the free state and a hydrated double salt of sodium sulphate and magnesium sulphate of the composition, $Na_2SO_4.MgSO_4.4H_2O$, commonly known as Astrakanite. The point x represents the composition of a quaternary invariant solution in equilibrium with three solids, sodium nitrate, Astrakanite and the sulphate-nitrate compound D. The addition of a small quantity of magnesium nitrate (or of magnesium sulphate) to the quaternary invariant solution x, in contact with the three solids with which it is in equilibrium will split up a portion of the solid compound D (nitrate-sulphate compound) into its respective components and the sodium sulphate thus produced will combine with the magnesium salts added to form Astrakanite setting free solid sodium nitrate. The mechanism of the phase reactions in equilibrium at the quaternary invariant point x will probably be as follows :

$$a.D + b.Mg(NO_3)_2 \rightleftharpoons c.x + d.D_1 + e.NaNO_3$$
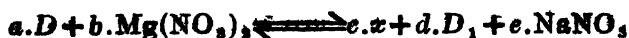
where a, b c, d, and e are any positive quantities of the substances that take part in the reaction and D and D_1 represent the sulphate-nitra te compound and Astrakanite respectively.

On the increasing additions of magnesium nitrate to the complex of the invariant solution x the above reaction will occur. This reaction will leave the actual composition of the solution x unaltered. When so much of the magnesium nitrate is added that it effects the complete conversion of the solid compound D into free sodium nitrate and Astrakanite, the compound D disappears as a solid phase and the composition of the solution alters along the curve xy.

From the above discussion it is clear that by maintaining a sufficient amount of the magnesium salts in the leaching solutions as well as in the raw material, the whole of the sulphate-nitrate compound can be decomposed, the sodium sulphate thus produced combining with magnesium sulphate to form Astrakanite leaving behind free sodium nitrate. If the amount of sodium sulphate exceeds the amount of magnesium sulphate (mol. for mol.), the excess of sodium sulphate will combine with sodium nitrate to form the sulphate-nitrate compound so that even if the quantity of magnesium salts added is insufficient to decompose the whole of the sulphate-nitrate

compound, it will greatly reduce the proportion of the sodium sulphate available to combine with sodium nitrate.

If heat is now abstracted from the solution by artificial refrigeration, it will cause the precipitation of pure or practically pure sodium nitrate if the temperature to which it is cooled is not so low as to effect the separation of magnesium nitrate present in the leaching solution.

It may be pointed out here that the solubility of sodium sulphate in nitrate liquors decreases with the rise of temperature and consequently this salt will not separate out on cooling up to a certain temperature, below which the hydrated sodium sulphate or Glauber's salt will come out. The point of transition may however be further lowered in the presence of certain salts, e.g., borates, iodates etc., which may be present in the raw material or which may be added to the leaching solution or to the solution after leaching and before refrigeration. The lowest temperature should not however be below that which would cause the precipitation of these salts. These salts, the object of which is simply to lower the transition temperature of sodium sulphate and Glauber's salt, are termed minor salts.

What has been said about Astrakanite is also true of other double sulphates, i.e., calcium potassium sulphate or Syngenite and calcium sodium sulphate or Glauberite. These are called 'protective compounds' since they protect the sodium nitrate from combining with sodium sulphate. The salts such as magnesium nitrate in the above example are termed 'stabilising agents', because in the presence of these salts the double sulphates are stabilised and remain insoluble.

The author is indebted to Professor F. G. Donnan for his very kind help and interest in this work.

nteraction of Sulphur Monochloride with Organic Compounds containing the reactive Methylene (—C₂H₂—) Group. Formation and Properties of Dithioketones (R₂C:S:S) and Dithioethers (R₂S:S). Part IV.

By Kuverji Gosai Naik and Yeshwant Narayan Bhat.

The work described in this communication is a continuation of he work already published by one of the authors (Naik, *J. Chem. Soc.*, 1921, **119**, 379, 1231; 1922, **121**, 2592). It was then suggested that sulphur monochloride appears to react in two forms:

$$(i) \ S = S \diagdown_{Cl}^{Cl} \quad \text{and} \quad (ii) \ \begin{array}{c} S-Cl \\ | \\ S-Cl \end{array}$$
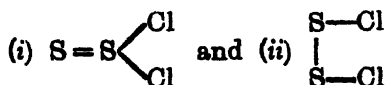
Whereas the formation of stable dithio-compounds points to the fact that S_2Cl_2 appears to react in form (ii), it would be indeed difficult to explain the formation of mustard gas on any other assumption than that sulphur monochloride reacts in form (i) (*loc. cit.*):

$$2 \ CH_2 : CH_2 + Cl_2 \ S:S \diagdown \begin{array}{l} (CH_2Cl.CH_2)_2 S:S \\ (CH_2Cl.CH_2)_2 S + S \end{array}$$
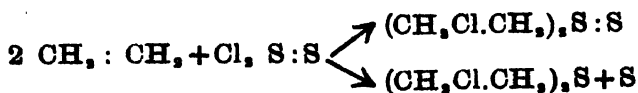
As reported before the dithio-grouping resulting from the interaction of sulphur monochloride with amides of malonic ester is very stable, for the resulting di-thioketones and dithio-ethers could be easily nitrated with fuming nitric acid without affecting the dithio-grouping.

The interactions of sulphur monochloride with (1) malon-di-ethyl-amide, (2) malon-di-n-propylamide, (3) malon-di-isobutylamide, (4) malon-di-n-heptylamide, (5) malon-di-m-toluidide and (6) methyl-malon-di-m-toluidide and (7) methyl malon-dibenzylamide were examined. Of these, malon-di-n-heptylamide, malon-di-m-toluidide and methyl-malon-dibenzylamide were prepared for the first time.

Whereas (a) compounds (1), (2), (3), (4) and (5) interacted to give dithioketones of the general formula

$$\begin{matrix} R \\ R \end{matrix} > C < \begin{matrix} S \\ S \end{matrix}$$
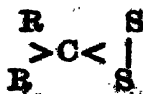
(b) compound (6) gave the dithio-ether of the general formula, $R \cdot C(CH_3) \cdot S \cdot S \cdot C(CH_3) \cdot R$.

Thus,

(a)
$$\begin{matrix} R \cdot NH \cdot CO \\ R \cdot NH \cdot CO \end{matrix} > CH_2 + \begin{matrix} Cl-S \\ Cl-S \end{matrix} \longrightarrow \begin{matrix} R \cdot NH \cdot CO \\ R \cdot NH \cdot CO \end{matrix} > C < \begin{matrix} S \\ S \end{matrix}$$

and

(b)
$$\begin{matrix} (R \cdot NH \cdot CO)_2 CHMe \\ (R \cdot NH \cdot CO)_2 CHMe \end{matrix} \begin{matrix} Cl-S \\ + \\ Cl-S \end{matrix} \longrightarrow \begin{matrix} (R \cdot NH \cdot CO)_2 - C(Me)S \\ (R \cdot NH \cdot CO)_2 - C(Me)S \end{matrix}$$
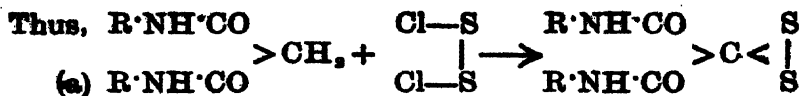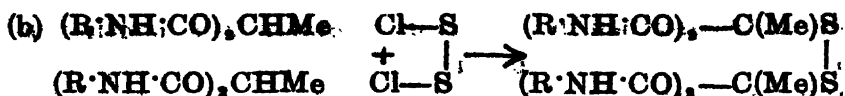
where R may be an ethyl, propyl, isobutyl, heptyl or tolyl group.

On nitration with fuming nitric acid, the dithio-compound derived from (5) gave a tetranitro-derivative, thus :

$$\begin{matrix} S \\ S \end{matrix} > C < \begin{matrix} CO \cdot NH \cdot C_7 H_7 \\ CO \cdot NH \cdot C_7 H_7 \end{matrix} \xrightarrow[HNO_3]{fuming} \begin{matrix} S \\ S \end{matrix} > C < \begin{matrix} CO \cdot NH \cdot C_7 H_5(NO_2)_2 \\ CO \cdot NH \cdot C_7 H_5(NO_2)_2 \end{matrix}$$
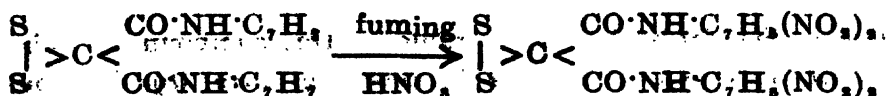
From this, it may be suggested that the dithio-grouping in compounds of the above type, may be structurally different from that present in $\beta\beta'$-dichlor-diethyldisulphide and such allied compounds. It also lends further support to the suggestion previously made, that sulphur monochloride may react in two forms (i) and (ii) and when it reacts in form (i), it gives rise to very stable dithio-compounds having the groupings

$$\begin{matrix} S \\ S \end{matrix} > C < \qquad \text{and} \qquad \begin{matrix} S-C- \\ S-C- \end{matrix}$$
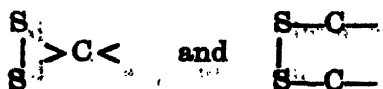
EXPERIMENTAL.

Interaction of Malon-diethylamide with Sulphur Monochloride.—Malon-diethylamide was prepared by Whiteley's method (*J. Chem. Soc.*, 1921, 119, 866) by the condensation of ethylmalonate (16 g.) with ethylamine (80 g. of 33 per cent solution). It was crystallised from benzene, m. p. 149°.

Malondiethylamide (2 g.) was put in a flask with 80 c.c. of dry benzene. Sulphur monochloride (2 g.) was added to it, and the flask was refluxed on a sand-bath for three hours. Hydrogen chloride began to evolve moderately on heating. Within 15 minutes, a solid separated, and bumping began which had to be controlled. The solid was separated by filtering the solution at the pump, and was washed with dry petroleum to remove the adhering sulphur monochloride.

It is very soluble in acetone, ethylacetate, acetic acid and chloroform; less so in methyl alcohol, ethyl alcohol, benzene and toluene; sparingly soluble in carbon tetrachloride, carbon bisulphide and ether, and insoluble in petroleum. It was crystallised from absolute alcohol. It shrinks at 186° and melts at 202°. (Found: N, 12·97; S, 29·46. $C_7H_{14}N_2O_2S_2$ requires N, 12·73; S, 29·09 per cent.).

*Malon-di-*n-*propylamide and Sulphur Monochloride.*—Malon-di-n-propylamide was prepared by Whiteley's method (*loc. cit.*). Ethylmalonate (9·5 g.) and n-propylamine were taken in a sealed tube and, after 24 hours, were heated at 125°—130° for six hours. The mixture solidified when allowed to remain at the ordinary temperature for some hours. The sealed tube was then opened, and the white solid was washed with petroleum. The m. p. of the substance, purified from benzene was 139°.

The above amide (5 g.) was condensed with sulphur monochloride (5 g.) in a similar way.

The product is very soluble in chloroform, benzene, ethylacetate, acetone, acetic acid and nitrobenzene; less so in ethyl alcohol, methyl alcohol and toluene; sparingly soluble in carbon bisulphide and ether; and insoluble in water and petroleum. It was crystallised from absolute alcohol. It shrinks at 172° and melts at 180°. (Found: N, 10·92; S, 25·69. $C_9H_{18}O_2N_2S_2$ requires N, 11·29; S, 25·80 per cent.).

Malon-di-isobutylamide and Sulphur Monochloride.—Malon-di-isobutylamide was prepared in the same way as malon-di-n-propylamide, by condensing ethylmalonate (8 g.) with isobutylamine (7·3 g.). The product was crystallised from benzene and melted at 126°.

The above amide (2 g.) and sulphur monochloride (1·5 g.) were condensed as in the previous cases.

The white product so obtained dissolves readily in chloroform, acetic acid, ethylacetate, or nitrobenzene; less readily in benzene, toluene, methyl alcohol, ethyl alcohol and acetone; sparingly so in ether, carbon bisulphide, or carbon tetrachloride, and is insoluble in hot water or light petroleum. It was crystallised from absolute alcohol. It shrinks at 196° and melts at 202°. (Found: N, 10·43; S, 22·98. $C_{11}H_{10}O_2N_2S_2$ requires N, 10·14; S, 23·19 per cent.).

Preparation of Malon-di-n-heptylamide.—A mixture of n-heptylamine (11·5 g.) and ethylmalonate (8 g.) was allowed to remain in a sealed tube at the ordinary temperature for 24 hours, when it was found in a semi-solid condition. The sealed tube was then heated in a paraffin bath at 125-130° for about 7 hours. The tube was opened when cool, and the white solid was taken out and washed with petroleum. The solid thus obtained was practically pure, and weighed 12 g.

It dissolves very readily in chloroform, benzene, toluene, ethylacetate, acetic acid, methyl alcohol, ethyl alcohol, acetone, and nitrobenzene; less readily in carbon tetrachloride and ether; and is sparingly soluble in petroleum, and insoluble in water. It crystallises from benzene and melts at 132°. (Found: N, 9·52. $C_{17}H_{34}O_2N_2$ requires N, 9·40 per cent.).

Malon-di-n-heptylamide and Sulphur Monochloride.—Malon-di-n-heptylamide (3 g.) was condensed with sulphur monochloride (1·5 g.) in the usual manner. The resulting substance, being very soluble in benzene, was precipitated by petroleum. It came out as a gelatinous white mass which was filtered and washed with dry petroleum.

It is very soluble in benzene, chloroform, acetic acid, methyl alcohol, ethyl alcohol, acetone, ethyl acetate and nitrobenzene; less soluble in toluene and carbon bisulphide; and sparingly soluble in ether, petroleum, and carbon tetrachloride. It was purified from alcohol, m. p. 125°. (Found: N, 7·83; S, 17·37. $C_{17}H_{32}O_2N_2S_2$ requires N, 7·77; S, 17·77 per cent.).

Malon-di-m-toluidide and Sulphur Monochloride.—The amide (2 g.) and sulphur monochloride (1 g.) were condensed as in the previous cases.

The product is readily soluble in chloroform, acetic acid, ethylacetate, acetone and nitrobenzene; less readily in benzene, toluene, methyl alcohol, ethyl alcohol, carbon tetrachloride and carbon

bisulphide; sparingly soluble in ether and hot water; and insoluble in light petroleum. It was crystallised from absolute alcohol. It shrinks at 158° and melts at 180° to a yellow liquid. (Found: S, 18·13. $C_{17}H$ $O_2N_2S_2$ requires S, 18·60 per cent.).

Nitration.—One gram of the above substance was added in a conical flask to 10 c.c. of fuming nitric acid (d 1·5). The flask was heated on a sand-bath until the evolution of oxides of nitrogen slackened. The flask was allowed to cool, when a little yellow solid came down. As the solid was too little to be filtered through the asbestos, the solution was added to some distilled water in a beaker. The precipitated solid was filtered at the pump, washed with distilled water, and allowed to dry at the ordinary temperature and powdered. The powder was dried in an air oven at 60-70°. It melts with decomposition at 166°. (Found: N, 16·32; S, 12·27. $C_{17}H_{13}O_{10}N_6S_2$ requires N, 16·03; S, 12·21 per cent.).

Methyl malon-di-m-toluidide.—Methylmalonic ester (10 g.) was condensed with m-toluidine (18 g.) in the same way as in the case of the corresponding malon-derivative. The temperature, in this case, was raised to 280°. The yield was very poor.

It is very soluble in benzene, toluene, chloroform, acetic acid, ethylacetate, methyl alcohol, ethyl alcohol, acetone and nitrobenzene; less readily in carbon tetrachloride, and insoluble in petroleum. It was crystallised from benzene, m. p. 157°. (Found: N, 9·86. $C_{18}H_{20}O_2N_2$ requires N, 9·46 per cent.).

Methyl malon-di-m-toluidide and Sulphur Monochloride.—The above amide (2 g.) and sulphur monochloride (0·5 g.) were condensed together in the usual manner. The reaction in this case was slower than in the case of the corresponding malon-di-m-toluidide derivative.

The white product is readily soluble in ethylacetate, acetic acid, acetone and nitrobenzene; less readily soluble in benzene, toluene, chloroform, carbon tetrachloride, methyl alcohol and ethyl alcohol; slightly soluble in carbon bisulphide, ether and hot water and insoluble in petroleum. It was crystallised from absolute alcohol, m. p. 187°-188°. (Found: S, 9·39. $C_{36}H_{38}O_4N_4S_2$ requires S, 9·78 per cent.).

Methylmalon-di-benzylamide.—Ethylmethylmalonate (9 g.) and benzylamine (11 g.) were taken in a round bottomed flask and heated

at 150-160° as in the case of ether amides. The white product so obtained readily dissolves in benzene, toluene, chloroform, methyl alcohol, ethyl alcohol, acetone, ethylacetate, acetic acid and nitrobenzene; less readily in chloroform, and is sparingly soluble in carbon bisulphide, ether, petroleum and hot water. It was purified from benzene, m. p. 142°. (Found: N, 9·66. $C_{18}H_{10}O_6N_2$ requires N, 9·46 per cent.).

CHEMISTRY DEPARTMENT,
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On the Reactivity of *ortho*-Diketonic Groups placed between two Nitrogen Atoms.

By Pran Kumar De and Anukul Chandra Sircar.

The original object of the investigation was to prepare azine derivatives by the condensation of diphenyl-thio-parabanic acid with *ortho*-diamines.
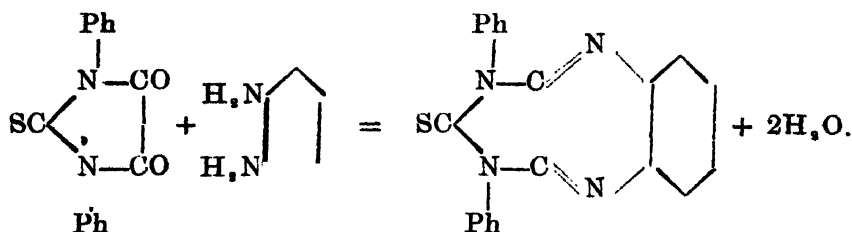
ortho-Phenylene and 1 : 2-napthylene diamines were tried, but, contrary to expectation, it was found that in either case the condensation products contained no sulphur. From this it was clear that the *ortho*-diketo groups, when placed between two nitrogen atoms behave quite differently than when placed between two carbon atoms, as in phenanthraquinone. In order to find out how far this assumption was true, the investigation was extended to some other *ortho*-diketo compounds of the same type, viz. dinitro-diphenylthio-parabanic acid, diphenyl parabanic acid, N-diphenyl-αβ-diketopiperazine and dimethyl-oxanilide.

It has now been found that none of them yield the expected azines. The three parabanic acids behave similarly towards the *ortho*-diamines, whilst N-diphenyl-αβ-diketo-piperazine and dimethyl oxanilide are without any action on them.

3

ortho-Phenylene diamine reacts with diphenyl-thio-parabani·
acid in the following way :

$$SC \Big\langle \begin{matrix} N \cdot \quad -CO \\ \vdots \\ N——CO \end{matrix} \quad + \ 2\ C_6H_4 \Big\langle \begin{matrix} NH_2 \ (1) \\ NH_2 \ (2) \end{matrix}$$

(with Ph on the upper N and Ph on the lower N)

$$= C_6H_4 \Big\langle \begin{matrix} NH—CO \\ \ \\ NH—CO \end{matrix} \quad + C_6H_4 \Big\langle \begin{matrix} NH \\ NH \end{matrix} \Big\rangle CS \ + \ 2C_6H_5NH_2$$

$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad \text{III}$$
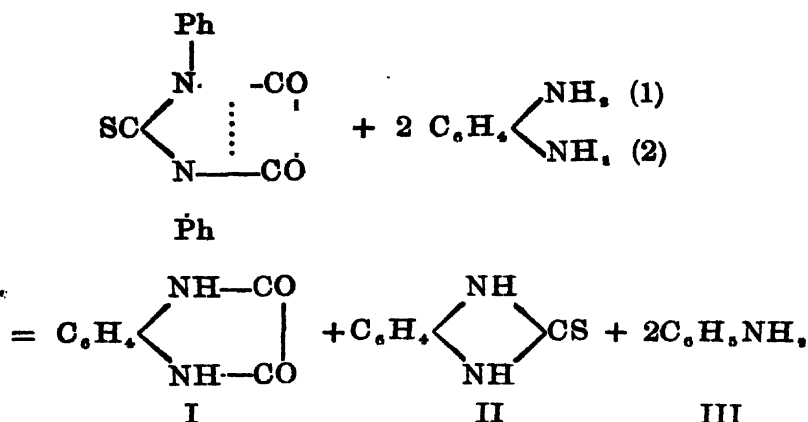
Of these the first and the third compounds were identified
in the reaction mixture, and the presence of the second compound
was proved by an indirect method.

The whole reaction probably proceeds as shown below :

$$(1)\quad SC \Big\langle \begin{matrix} N—CO \\ | \\ N—CO \end{matrix} \ \begin{matrix} H_2N \\ \\ H_2N \end{matrix} \Big\rangle C_6H_4 \ = C_6H_4 \Big\langle \begin{matrix} NH—CO \\ | \\ NH—CO \end{matrix} + SC \Big\langle \begin{matrix} NH \cdot Ph \\ NH \cdot Ph \end{matrix}$$

(with Ph on upper and lower N)

$$(2)\quad SC \Big\langle \begin{matrix} NH \cdot Ph \\ NH \cdot Ph \end{matrix} \ \begin{matrix} H_2N \\ \\ H_2N \end{matrix} \Big\rangle C_6H_4 = SC \Big\langle \begin{matrix} NH \\ NH \end{matrix} \Big\rangle C_6H_4 \ + \ 2PhNH_2$$
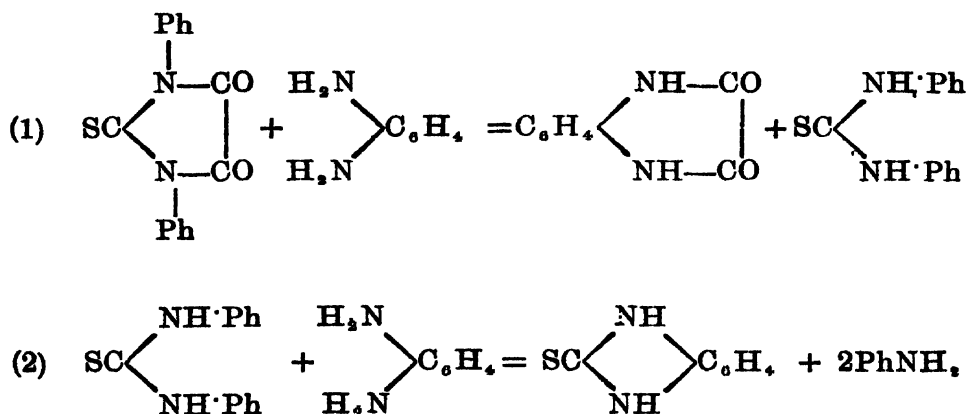
That the second reaction is possible has been proved by a blank
experiment with thiocarbanilide *ortho*-phenylene diamine and it
has been found that the reaction between them proceeds exactly in
the way as shown above.

In the case of diphenyl-parabanic acid the reaction does not
proceed up to the second stage. From the reaction mixture both
phenylene-oxamide and S-diphenyl urea were isolated and no aniline
could be traced.

EXPERIMENTAL.

Condensation of Diphenyl-thio-parabanic Acid with ortho-*Phenylene diamine.*

A mixture of diphenyl thio-parabanic acid (1 g.) and *ortho*-phenylene diamine (1 g.) dissolved in pyridine (8 c.c.) was boiled for a few minutes. The separated solid was filtered and crystallised from hot water in fine silky needles, not melting below 300°. It was slightly soluble in alcohol, soluble in hot water, acetic acid or pyridine, and was identified to be phenylene-oxamide. (Found: N, 17·15. Calc: N, 17·28 per cent.).

The pyridine solution, on dilution with water, separated a tarry substance, from which nothing could be isolated. The presence of aniline in the filtrate from the above was proved by diazotisation and coupling with β-naphthol.

1 : 2-Naphthylene diamine behaved exactly in the same way giving naphthylene-oxamide.

Condensation of Thio-carbanilide with ortho-*Phenylene diamine.*— The clear solution obtained by heating for three minutes a mixture of thio-carbanilide (3 g.), *ortho*-phenylene-diamine (1·5 g.) and pyridine (3 c.c.), yielded on cooling a solid mass. This was filtered and crystallised from hot water in colourless prisms, m. p. 295-297° (A). It is soluble in alkali but insoluble in acid.

The pyridine solution, on dilution with water, separated a tarry mass which soon solidified on acidification with dilute hydrochloric acid. It was purified by crystallization (prisms) from alcohol using a little bone charcoal ; m. p. 294-296° (identical with A.)

The substance was identified to be phenylene-thio urea (Found: N, 18·15. Calculated: N, 18·66 per cent.).

The filtrate was diazotised and treated with an alkaline solution of β-naphthol when a red precipitate separated. This was crystallised from alcohol as shining red needles, m. p. 134° and identified to be benzene-azo-β-naphthol.

Dinitro-diphenyl-thio-parabanic acid behaved exactly in the same way as diphenyl-thio-parabanic acid. From its reaction mixture with *ortho*-phenylene diamine, phenylene oxamide and *meta*-nitraniline were isolated.

Condensation of Diphenyl parabanic Acid with ortho-*Phenylene* *diamine.*—The precipitate, which separated on boiling for five minutes a mixture of diphenyl-parabanic acid (1 g.) and *ortho*-phenylene diamine (1 g.) dissolved in pyridine (5 c.c.), crystallised from hot water in colourless silky needles, not melting below 800°. The substance was identified to be phenylene oxamide.

The filtrate on dilution with water yielded a white precipitate, which crystallised from alcohol in rectangular plates, melting at 238°. The substance was identified to be *S*-diphenyl-urea. This was confirmed by a mixed melting point determination.

All attempts to condense *ortho*-phenylene-diamine with *N*-diphenyl-*αβ*-diketopiperazine and dimethyl oxanilide even by boiling for one hour in pyridine solution failed and the diketo compounds were recovered unchanged in each case.

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  DACCA UNIVERSITY,
    DACCA.

Rubiadin. Part I. Synthesis of 1-Methyl-2:4-dioxy-anthraquinone.

BY PRAFULLA CHANDRA MITTER, MONMOHAN SEN AND
PRAFULLA KUMAR PAUL.

Rubiadin was first isolated and studied by Schunck and Marchlewski (*J. Chem. Soc.*, 1893, **63**, 969). They obtained it by the hydrolysis of rubiadin-glucoside, which occurs in madder-root, *Rubia Tinctorum*. It is a lustrous yellow substance, m.p. 290° and sublimes unchanged when heated further. The analysis of the substance as well as the molecular weight determination by Raoult's method agree with the formula $C_{15}H_{10}O_4$. It is an anthraquinone derivative and closely resembles purpuroxanthin as revealed by spectroscopic examination. This leads to the conclusion that rubiadin is a methylated purpuroxanthin. The absence of any methoxy group points to the methyl group being contained in the nucleus. Again since on oxidation phthalic acid is obtained (*J. Chem. Soc.*, 1894, **65**, 18), the methyl and hydroxyl groups must lie in the same benzene ring of the anthraquinone complex. This restricts the choice of a formula for rubiadin between (1) 2-methyl-1:3-dioxy-anthraquinone and (2) 1-methyl-2:4-dioxy-anthraquinone. Schunk and Marchlewski synthesised (1) by condensing 2:6-dioxy-*para*toluic acid with benzoic acid in presence of sulphuric acid (*J. Chem. Soc.*, 1894, **65**, 183) and obtained a substance melting at 282° and when quickly heated at 290° and giving an acetyl derivative, m.p. 217°-218°. Rubiadin melts at 290° and its acetyl derivative melts at 225°. On these grounds Schunck and Marchlewski gave formula (2) to rubiadin.

The main object of the work was to verify this by actual synthesis.

Fritsch has found that 3-methoxybenzoic acid methyl ester (*Annalen*, 1897, **296**, 344) and methyl 2:3-dimethoxy benzoate (*Annalen*, 1898, **301**, 352) condense readily with chloral in presence of sulphuric acid to give trichloromethyl phthalides, from which the corresponding phthalic acids may be easily prepared. The reaction

has been successfully applied by Meldrum and others (*J. Chem. Soc.*, 1911, **99**, 1712; 1920, **117**, 964; 1921, **119**, 201) for converting oxybenzoic acids to the corresponding phthalic acids.

Our object was to apply this reaction to 2-methyl-3:5-dimethoxy benzoic acid methyl ester with a view to prepare the corresponding phthalic acid, $C_6H(CH_3)(OCH_3)_2(COOH)_2$. The anhydride of this acid on condensation with benzene in presence of anhydrous aluminium chloride and subsequent ring closing with sulphuric acid was expected to give 1-methyl-2:4-dimethoxyanthraquinone, the demethylation product of which would have the constitution ascribed to rubiadin by Schunck and Marchlewski. It was found that the reaction proceeds fairly smoothly up to the phthalide,
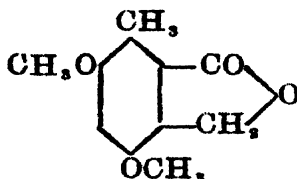
The phthalides can be prepared from phenolic ether acids directly by condensing with formaldehyde in presence of hydrochloric acid (*J. Chem. Soc.*, 1925, **127**, 195) and this method was employed for preparing large quantities of phthalide from cresorsellenic acid for oxidation experiments. All our attempts to oxidise the phthalide to the corresponding phthalic acid have, however, so far, failed.

We next had recourse to another method of preparation of anthraquinone derivative for our present purpose. 3:5-Oxybenzoic acid condenses with *p*-toluic acid (*J. Chem. Soc.*, 1893, **63**, 1141) and 4-methyl-3:5-dioxybenzoic acid (*J. Chem. Soc.*, 1894, **65**, 182) and 3:5-dioxybenzoic acid (*Annalen*, 1887, **241**, 266) condense with benzoic acid in presence of concentrated sulphuric acid to give rise to the corresponding anthraquinone derivatives. This method was successfully applied to 2-methyl-3:5-dioxybenzoic acid (cresorsellenic acid) with the result that it is now definitely established that the constitution of rubiadin is not what Schunck and Marchlewski ascribed to it.

<div align="center">EXPERIMENTAL.</div>

2-Methyl-3:5-dioxybenzoic Acid (Cresorsellenic Acid).—The acid was prepared according to the method of Jacobsen and Wierss (*Ber.*, 1888, **16**, 1960) with slight modification. *o*-Toluic acid (50 g.) was treated with fuming sulphuric acid (200 g.) containing 65% of

sulphuric anhydride and the reaction mixture was heated in an oil-bath at 160-170° for 12 hours. The fuming sulphuric acid was added in two instalments (150 g. and 50 g.) and the heating was completed in two days. The cold sulphonation product was poured on crushed ice and the disulphonic acid was separated from sulphuric acid as the soluble calcium salt by treatment with calcium carbonate, boiling and filtering. The filtrate was then treated with potassium carbonate, when calcium carbonate was precipitated, and the potassium disulphonate remained in solution. It was concentrated by heating on a bare flame and ultimately evaporated to dryness on the water-bath. The yield of the potassium salt was almost theoretical.

The potassium salt—50 g. being taken at a time—was added gradually to three times its weight of fused potassium hydroxide kept in a silver basin at a temperature of 210°, and stirred constantly with a copper tube closed at one end and fitted up with a thermometer, which dipped in melted paraffin kept in the tube. The addition of potassium disulphonate was completed in half an hour and the melt was then heated at 248-250° for another half an hour and then the temperature was gradually raised to 270° when the reaction was complete.

The product of potash fusion was then made into a paste with powdered ice and treated with excess of concentrated hydrochloric acid. The acidified solution thus obtained was then allowed to cool, and, was filtered and extracted thrice with ether. Cresorsellenic acid was obtained on evaporation of the ether as a grey coloured solid mass mixed up with tarry matters. The mass was dried on a porous plate and crystallised from water with the addition of animal charcoal when a granular white crystalline product was obtained; m. p. 237-239°. Yield of the substance was 30% of the theoretical.

2-Methyl 3:5-dimethoxybenzoic acid (cresorsellenic acid dimethyl ether), prepared with the help of dimethyl sulphate in the usual manner, formed white needle shaped crystals, m. p. 160°. The yield was 90% of the theoretical. (Found: C, 60·91; H, 6·31. $C_{10}H_{12}O_4$ requires C, 61·22; H, 6·12 per cent.).

2-Methyl-3:5-dimethoxybenzoic acid methyl ester (methyl ester of cresorsellenic acid dimethyl ether), b. p. 289-291°. (Found: C, 62·55; H, 6·92. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·66 per cent.).

6-Methyl-3:5-dimethoxy-2-trichloromethyl phthalide.—2-Methyl 3:5-dimethoxybenzoic acid methyl ester. (5 g.) was mixed with finely powdered chloral hydrate (4 g.) in a stoppered bottle

and cold 90% sulphuric (25 g.) acid was added and the mixture allowed to stand for 24 hours. The reaction was then complete, and the condensation product was found to be a dirty solid mass, which was mixed up with pieces of ice and filtered. The solid mass thus obtained was washed with water and 50% alcohol alternately to remove the unacted reactants and the sulphuric acid. The crude condensation product was then dried on the porous plate and crystallised from methyl or ethyl alcohol. White crystalline mass, m. p. 176°. The yield was theoretical. (Found: Cl, 32·39. $C_{12}H_{11}O_4Cl_3$ requires Cl, 32·71 per cent.).

6-Methyl-3:5-dimethoxy-2-phthalide carboxylic Acid.

The trichloromethyl phthalide derivative (5 g.) was heated with an excess of 20% caustic soda solution (25 c. c.) on the water-bath with a reflux condenser for 5 hours. The trichlorophthalide dissolved very slowly, ultimately giving a clear homogeneous yellowish liquid. The solution was then cooled and exactly neutralised, and to the neutral solution a very slight excess of hydrochloric acid was added when a tarry matter together with a little of the product of hydrolysis of the trichloromethyl phthalide was thrown down which was filtered off. The filtrate was then acidified with a slight excess of hydrochloric acid and the phthalide carboxylic acid, which was precipitated as sticky white precipitate, was filtered at the pump and dried on the porous plate. It is soluble in water with difficulty but readily in alcohol. It is crystallised repeatedly from water and purified by animal charcoal. White crystalline plates, m. p. 218-219°. Yield, 50%. During an attempt to crystallise the acid from alcohol the ethyl ester melting at 134° was obtained. (Found: C, 52·9 ; H, 5·5. $C_{12}H_{16}O_6$ requires C, 57·14 ; H, 4·76. $C_{12}H_{12}O_6, H_2O$ requires C, 53·3 ; H, 5·1 per cent).

6-Methyl-3:5-dimethoxyphthalide.—

Phthalide carboxylic acid (2 g.) was taken in a large test tube fitted with a long air condenser and heated in a sulphuric acid bath at 225-235°. The decomposition of the acid to the phthalide was complete when no more carbon dioxide evolved ; but to ensure a complete decomposition it was heated for sometime longer even when the evolution of CO_2 had ceased. A long air condenser was used because the phthalide formed in the process is highly sublimable. The phthalide is slightly soluble in alcohol, but fairly soluble in chloroform. A very suitable solvent for the phthalide is found in acetic acid. It is a very light crystalline white substance melting at 249°. The yield in this process was

as low as 20% of the theoretical. (Found: C, 62·9; H, 5·96. $C_{11}H_{12}O_4$ requires C, 68·45; H, 5·76 per cent.) Attempts at oxidation of the phthalide to the corresponding phthalic acid have so far failed.

1-*Methyl*-2 : 4-*dioxyanthraquinone*.—2-Methyl-3 : 5-dioxybenzoic acid (cresorsellenic acid, 5 g.) was intimately mixed with pure benzoic acid (50 g.) in a 500 c. c. round bottomed Pyrex flask. To the mixture chemically pure sulphuric acid (25 g.) was added and gently shaken, when a homogeneous red solution was formed. Such a large excess of benzoic acid was used to avoid the self condensation of the cresorsellenic acid. The reaction mixture was heated in an oil-bath at 125—180° for 12 to 15 hours. The heating was completed in 2 days. As the heating was continued the colour of the reaction mixture changed from red to dark-red and ultimately to black. When the reaction was complete, the cold reaction-product was poured on powdered ice, filtered and dried on the porous plate. The product thus obtained contained a large amount of carbonaceous matter from which the substance was separated by extraction with ether in a Soxhlet apparatus. The ether was then removed by distillation, when a brown solid mass of the anthraquinone derivative mixed up with benzoic acid was obtained. The benzoic acid could be removed from the condensation product by steam distillation, but the process was found to be inconvenient because nearly 12 hours were necessary to completely drive away the benzoic acid. By using Na_2CO_3 solution to effect the separation the difficulty was overcome. The self-condensation product of cresorsellenic acid (anthrachrysone) contains four OH groups, and is much more acidic than the dihydroxyanthraquinone. The crude condensation product was taken in a mortar and triturated with Na_2CO_3 solution which was very gradually added so long as there was evolution of CO_2. When no further CO_2 evolved a very small quantity of Na_2CO_3 solution was very cautiously added to partially dissolve the anthrachrysone, and the substance was separated by filtration. The crude anthraquinone derivative thus obtained was then crystallised two times from benzene when a very beautiful orange crystalline product melting, after sublimation, at 265-266° was obtained. Yield was 4% of the theoretical. (Found: C, 70·52; H, 4·22. $C_8H_{10}O_4$ requires C, 70·86; H, 3·80 per cent).

1-*Methyl*-2 : 4-*diacetoxyanthraquinone*.—1-Methyl-2 : 4-dioxyanthraquinone (·5 g.) was mixed with an excess of freshly distilled acetic anhydride and a few drops of pyridine, and taken in a small conical flask fitted with a long air condenser and heated to

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boiling on the sand-bath very gently for an hour and a half, by which time the reaction was complete. The product was then poured into water. The acetyl derivative was at first thrown down as an oily liquid which solidified on cooling. The solid product was then separated by filtration, and purified from associated acetic anhydride and the unacted anthraquinone derivative by repeated treatment with sodium carbonate solution. The product was then washed with cold water to remove the adhering sodium carbonate, dried on the porous plate and purified by crystallisation from alcohol with animal charcoal, when the di-acetyl derivative was obtained as faintly yellowish needle shaped crystals, m. p. 181-182°. (Found: C, 67·49; H, 4·43. $C_{19}H_{14}O_6$ requires C, 67·45; H, 4·14 per cent.).

On deacetylation, the original substance meeting at 265-266° was obtained.

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The Constitution of Vasicine. Part I. A Synthesis of 2-Propyl-(*iso*propyl)-4-oxyquinazoline.

By Ananta Kumar De and Jnanendra Nath Ray.

In connection with certain investigations proceeding in this laboratory for a number of years it was found that urethanes condensed easily with acylamines in presence of phosphoric oxide and phosphorous trichloride to give substituted quinazolines (Cf. Sen and Ray, *J. Chem. Soc.*, 1926, **129**, 646). In the meantime, a paper appeared (This *Journal*, 1927, **4**, 1) in which Ghosh claims that the active principle of *Adhatoda vasica* is represented by (I).

I
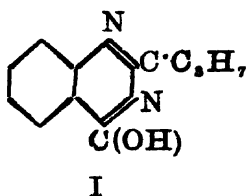
It seemed to the present authors that such a structure, apart from other considerations, does not seem to be very probable because the oxidation reaction on which it was mainly based is not entirely satisfactory. There is nothing very improbable intrinsically in an alkaloid having a quinazoline structure, as quite a few are known to belong to this class, *e.g.*, cytosine, thymine, etc. But they are of animal origin. But however, recently evodiamine, rutaecarpine (*cf.* Asahina, Manske and Robinson, *J. Chem. Soc.*, 1927, **131**, 1708) have been shown to fall under this group. Therefore, it was deemed that a direct comparison of the natural product with a compound synthesised, having the formula (I) depicted above, would place the matter beyond any reasonable doubt. The opportunity to do so arose now that the technique of Sen and Ray's quinazoline synthesis has been satisfactorily developed and we encountered no difficulty in condensing butyranilide and *iso*butyranilide with urethane in xylene

solution with phosphoric oxide as the condensing agent.   The reaction took place thus :

$$\text{NH}$$

$$\begin{array}{c} \text{NH} \\ \diagup \\ \text{CO·C}_3\text{H}_7 \\ +\text{OEt·CO·NH}_2 \end{array} = \begin{array}{c} \text{NH} \\ \diagup \\ \text{C·C}_3\text{H}_7, +\text{H}_2\text{O}+\text{EtOH} \\ \text{N} \\ \text{CO} \end{array}$$

$$\rightleftharpoons \begin{array}{c} \text{N} \\ \diagup \\ \text{C.C}_3\text{H}_7, \\ \text{N} \\ \text{C(OH)} \end{array}$$
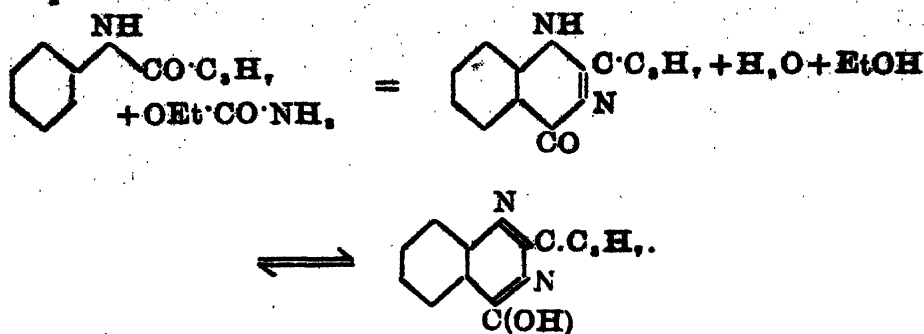
The product was a monacid base and was purified by redissolution in acid and precipitation with alkali and then finally twice crystallising from boiling alcohol (charcoaled).   The product from butyranilide, *i.e.*, where C_3H_7 is *n*-propyl, melted at 197°, whilst a specimen of the natural product, which we purified from a crude specimen kindly supplied by Messrs. Sen and Ghosh of Dehra Dun, melted at 196°.   Ghosh states 190-191° (with decomposition) as the m. p. of vasicine.   The two substances obviously have m. p.'s quite close to each other, but a mixture of the two melts indefinitely from 160° upwards.   We prepared a picrate of our synthetic base but the m. p. was 184° whilst that of the natural base is 199°.   Clearly therefore the two substances are not identical.

Next we prepared the *isopropyl* analogue starting from *isobuty*ranilide but the base obtained in this case melted at 227°.   A mixture with the natural base melted indefinitely from 175°.   The m. p. of the picrate of our synthetic base is 215-216° and its mixture with that from natural base melted indefinitely.   Therefore we are inclined to think that the structure advanced by Ghosh (*loc. cit.*) for vasicine is not the correct representation of its constitution.

For the purpose of these comparisons we obtained the crude vasicine from Dehra Dun but we had to take recourse to an elaborate scheme of purification (detailed in the experimental part).   The melting point now recorded of the base is higher than that quoted by Sen and Ghosh.   The purified base is almost odourless.

<center>EXPERIMENTAL.</center>

<center>*Purification of Crude Vasicine (from natural sources).*</center>

About 8 g. of the crude base is refluxed for about an hour with 50 c.c. of pure dry benzene.   The extract is cooled and filtered.   A

considerable quantity of resinous material is left undissolved. To the solution is added just sufficient ether to cause a slight turbidity when a further quantity of impure material comes down. This is removed and the solution is then diluted with more ether and is left to crystallise. The sides of the vessel are scratched from time to time and the vasicine crystallises out. This is collected and thrice crystallised from boiling alcohol with the aid of charcoal, m. p. 198° with decomposition. The crystals have a very pale buff colour but appear perfectly colourless in contact with the solvent. The substance is very sparingly soluble in alcohol in the pure state. The base dissolves in cold sulphuric acid without a colour, a .drop of nitric acid imparts a yellow colour to the solution which, however, is discharged on dilution. The substance, on being heated in a dry test tube, decomposes and a basic gas is evolved. This does not seem to be ammonia but is not unlike dimethylamine in many respects. This cannot be emphasised at this stage because the material we had at our disposal was really too small. But we hope to characterise this later and we believe that this will ultimately throw considerable light on the constitution of the alkaloid.

Butyranilide.—Butyric acid (1 mol.) and aniline (1 mol.) with a few drops of pyridine were refluxed for 3 hours when the reaction was complete. The product was poured in much water (cold) whereupon the anilide separated out in crystals. Crystallised from hot dilute alcohol, m. p. 92° (*cf.* Gerhard, *Annalen*, 1858, **87**, 166) m. p. 90°). Yield 80 g. from 40 g. of butyric acid.

Condensation of Butyranilide and Urethane.—Butyranilide (29 g.) and urethane (16 g.) in xylene (50 c.c.) were refluxed very gently (140-145°) for 4 hours with phosphoric oxide (15. g.). From the cooled product xylene was completely decanted off and the residue was dissolved in water cautiously. The solution freed from insoluble matter was cooled with ice and basified with dilute sodium hydroxide solution (cold). The thick white precipitate of the basic product is filtered and freed from alkaline mother-liquor. It is then dissolved in dilute hydrochloric acid and reprecipitated with alkali. The crude base thus obtained was then twice crystallised from boiling absolute alcohol (about 50 c.c.) with the aid of charcoal in long thin needles, m. p. 197°. Yield 20 g. (Found: C, 70·8; H, 6·5; N, 14·96. $C_{11}H_{14}ON_2$ requires C, 70·2; H, 6·4; N, 14·9 per cent.). A mixture of this substance with an equal amount of vasicine melts indefinitely from 160°.

Preparation of the Picrate.—The synthetic base (1 g.) in alcohol (20 c.c.) was heated for sometime on the water-bath with an alcoholic solution of picric acid (1 g. in 20 c.c.) under reflux. The cooled product deposited fine cubical crystals of the picrate. These were collected and recrystallised from alcohol ; m. p. 184°. (Found: N, 16·2. $C_{17}H_{15}N_5O_8$ requires N, 16·8 per cent.).

Action of Methyl Iodide on the Synthetic Base.—The base (1 g.) in methyl alcohol (10 c.c.) and excess of methyl iodide were refluxed, as prescribed by Sen and Ghosh (*loc. cit.*) for vasicine methiodide, for 2 hours on the water-bath. The cooled mixture deposited, however, the original substance unchanged. Therefore the synthetic base does not form a methiodide under the same conditions as vasicine does.

isoButyranilide.—This substance was prepared following the conditions detailed under butyranilide. The product, however, was poured on to only a small amount of cold saturated brine. The substance crystallised out on standing and had m. p. 101°. (*Cf.* Norton, *Amer. Chem. J.*, 1885, 7, 117, who gives m. p. 102°·5).

Condensation of isoButyranilide and Urethane: Formation of 2-isoPropyl-4-oxy quinazoline.—A mixture of *iso*butyranilide (15 g.), urethane (10 g.) xylene (40 c.c.) and phosphoric oxide (10 g.) was heated at 140° in an oil-bath for 5 hours. Xylene was decanted off from the reaction mixture at the end of, the reaction. The residue was dissolved in water and filtered. The filtrate was strongly cooled and carefully basified with cold dilute sodium hydroxide solution. The precipitated basic material was redissolved in dilute hydrochloric acid and reprecipitated with dilute alkali solution. It was finally crystallised several times from absolute alcohol in which it is sparingly soluble as fine long needles, m. p. 227° (with decomposition). (Found: N, 15·3. $C_{11}H_{12}ON_2$ requires N, 14·9 per cent.). A mixture of this base with natural vasicine melted indefinitely from 175° to 200°.

Picrate of the Base.—This was prepared exactly as the corresponding compound from the *n*-propyl analogue. The picrate crystallises in short stout yellow prisms, m. p. 215-216°. (Found: N, 17·04. $C_{17}H_{15}N_5O_8$ requires N, 16·8 per cent.).

Action of Methyl Iodide on the Base.—Following the procedure adopted by Sen and Ghosh, we found, on similar treatment, our synthetical base to be unchanged.

The two synthetic bases did not show the colour reaction noted in the case of natural vasicine.

In conclusion, we wish to thank Prof. Sir P. C. Rây for his very kind interest in the work, and also we wish to place on record our gratitude to Dr. J. N. Sen and Mr. T. P. Ghosh for their courtesy in giving us a specimen of (crude) vasicine.

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P. S.—Since the above was in print our attention was drawn to the compound 4-oxy-2-propylquinazoline (I) by Bischer and Lang (Ber., 1895, 28,287). These authors state its m.p. to be 205°, whilst ours melts at 167°. Its difference from natural vasicine should be an apriori argument against the structure (J) for the latter. The corresponding isopropyl compound described by Nimentowski (J.pr. Chem., (2) 51, 569) melts at 234°. This seems to be identical with our product, the m.p. of which however was found to be 3° higher than that recorded by Nimentowski.

The identity of both these quinazoline derivatives with ours proves at the same time that cyclic amidines are really obtained by Sen and Rây's method.

Condensation of Cyanacetic Ester with some Aryl and Alkylamines. Preparation of some Aryl and Alkyl substituted Cyanacetamides.

By Kuverji Gosai Naik and Yeshwant Narayan Bhat.

The method adopted in the preparation of these compounds was a modification of that employed by Freund (*Ber.*, 1884, **17**, 134) and Whiteley (*J. Chem. Soc.*, 1903, **83**, 24), in the preparation of malondiphenylamide.

Cyanacetanilide [*Compt. rend.*, 1895, **121**, 189 ; Quenda, *Chem. Centr.*, 1892, i, 383 from *Atti. R. Accad. Sci. Torino*, 27 ; Warapsky and Hillers, *J. pr. Chim.*, (ii), **92**, 297], cyanacet-*p*-toluidide (Grothe, *Arch. Pharm.*, **238**, 608 ; Haller, *Compt. rend.*, 1889, **108**, 1116), cyanacetbenzylamide (Guareschi, *Chem. Centr.*, 1892, i, 382 from *Atti R. Accad. Sci. Torino*, 27) and cyanacetxylidide (m. p. 167°) are already known.

(1) *Cyanacet-*o*-toluidide, (2) cyanacet-*m*-toluidide (3) cyanacet-*a*-naphthylamide, (4) cyanacet-β-naphthylamide, (5) cyanacet-*adj.*-*m*-xylidide, (6) cyanacetmethyl-amide and (7) cyanacetethylamide were prepared for the first time. The methods employed had to be varied with the varying basic nature of the amines, more drastic method being employed in the case of those amines which possessed feeble ammoniacal characteristics.

Benzylamine resembles, though remotely, the paraffin amines and hence the method of preparing an amide with the help of this amine has to be modified from that adopted in the previous cases. Aniline, toluidines and naphthylamines possess ammoniacal characteristics to a very feeble extent indeed, and in their cases, more drastic methods for the production of the substituted derivatives were employed. We can thus roughly divide the preparations of the amides into three divisions :—

A. Cyanacetmethylamide; cyanacetethylamide.

B. Cyanacetbenzylamide.

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C. Cyanacetanilide ; cyancet-*p*-toluidide ; cyanacet-*o*-toluidide ; cyanacet-*m*-toluidide ; cyanacet-*α*-naphthylamide ; cyanacet-*β*-naphthylamide ; cyanacet-*adj.*-*m*-xylidide.

Of the above substituted amides, cyanacetanilide, cyanacet-*p*-toluidide and cyanacetbenzylamide are known, but no reliable details of the methods employed in their preparations could be found. The melting points of these substances fairly agree with those reported and the analyses confirm the percentage of nitrogen required.

<div align="center">EXPERIMENTAL.</div>

Preparation of Substituted Amides of Cyanacetic Ester.

In the preparation of substituted amides of the aromatic series Whiteley's method (*J. Chem. Soc.*, 1903, **83**, 24) with the modification described by Naikl (*J. Chem. Soc.*, 1921, **119**, 379) was followed.

Cyanacetanilide.—Ethyl cyanacetate (37 g.) and pure redistilled aniline (45 g.) were mixed together in a round-bottomed flask provided with a wide upright bent tube, one end of which passed through a cork in the mouth of the flask, and the other end was attached to the condenser. The flask was kept at 160°—170° for six hours. The height of the upright portion of the bent tube was so adjusted that for every drop of alcohol distilled over, a dozen drops of the liquid went back to the flask. This was to avoid any of the reacting liquids coming over unchanged. The temperature was slowly raised to 180° till no more alcohol came over. The contents of the flask, when hot, were then poured into a porcelain mortar where the whole solidified. The colour of the liquid when taken out of the bath was red. The solid cake was broken and triturated with a mixture of equal volumes of benzene and light petroleum, and filtered at the pump. The process was repeated until the reddish colour of the solid disappeared. The yield was 66 per cent.

Cyanacetanilide is readily soluble in methyl alcohol, ethyl alcohol, acetone, acetic acid, ethyl acetate and nitrobenzene ; less readily so in benzene, toluene, chloroform and hot water ; and insoluble in light petroleum (b. p. 50-60°), carbon tetrachloride, carbon disulphide and xylol. It was crystallised from alcohol as white needles,

m. p. 198-199°. (Found: N, 17·68. $C_9H_8N_2O$ requires N, 17·50 per cent.).

Cyanacet-p-toluidide.—Cyanacet-p-toluidide was prepared from ethyl cyanacetate (20 g.) and freshly distilled p-toluidine (21 g.) in the same way as cyanacetanilide.

The white product so obtained is readily soluble in methyl alcohol, ethyl alcohol, acetic acid, ethyl acetate, acetone and nitrobenzene, less so in benzene, toluene and chloroform; sparingly soluble in carbon tetrachloride and hot water, and insoluble in ether, light petroleum and carbon bisulphide. It was crystallised from alcohol, m.p. 180°. (Found: N, 15·71. $C_{10}H_{10}N_2O$ requires N, 16·09 per cent.).

Cyanacet-o-toluidide.—Ethyl cyanacetate (34 g.) and o-toluidine (29 g.) were condensed together in a similar way.

The white product is readily soluble in benzene, toluene, methyl alcohol, ethyl alcohol, ethyl acetate, acetic acid, chloroform, acetone and nitrobenzene; less readily so in carbon tetrachloride, very sparingly soluble in hot water and petroleum, and insoluble in carbon bisulphide and ether. It was crystallised from alcohol as thin plates, m. p. 125°. (Found: N, 15·90. $C_{10}H_{10}N_2O$ requires N, 16·09 per cent.).

Cyanacet-m-toluidide.—Ethyl cyanacetate (15 g.) and m-toluidine (13 g.) were condensed in the usual manner. The solid was triturated and washed with ether.

It is readily soluble in methyl alcohol, ethyl alcohol, acetic acid, ethyl acetate, acetone and nitrobenzene; less readily in benzene, toluene, chloroform and hot water; sparingly soluble in carbon tetrachloride, carbon bisulphide and ether; and insoluble in petroleum. It separated from benzene in the form of white needles, m. p. 132°. (Found: N, 16·25. $C_{10}H_{10}N_2O$ requires N, 16·09 per cent.).

Cyanacet-a-naphthylamide.—Ethyl cyanacetate (22 g.) and a-naphthylamine (25 g.) were similarly condensed. The product was finally washed with alcohol until the reddish colour of the solid was removed.

It is freely soluble in ethylacetate, acetic acid, acetone, and nitrobenzene; less soluble in methyl alcohol, ethyl alcohol, benzene,

toluene and chloroform; sparingly soluble in carbon tetrachloride, carbon bisulphide, petroleum, ether and hot water. It was crystallised from acetic acid, m. p. 175°. (Found: N, 13·65. $C_{13}H_{10}N_2O$ requires N, 13·33 per cent.).

Cyanacet-β-naphthylamide.—Ethyl cyanacetate (25 g.) and β-naphthylamine (22 g.) were condensed as in the previous cases.

- The white solid so obtained is very soluble in ethyl acetate, acetic acid, acetone and nitro-benzene; less so, in benzene, toluene, chloroform, hot water and methyl alcohol, ethyl alcohol; sparingly soluble in carbon tetrachloride, carbon bisulphide, and ether; and insoluble in light petroleum. It was crystallised from alcohol, m. p. 174°. (Found: N, 13·18. $C_{13}H_{10}N_2O$ requires N, 13·33 per cent.).

*Cyanacet-*adj-m-*xylidide.*—Ethyl cyanacetate (11 g.) and *adj-m*-xylidine (12 g.) were condensed in the usual manner. The product is readily soluble in ethyl acetate, acetic acid, methyl alcohol, ethyl alcohol, acetone and nitrobenzene; less so in benzene, toluene and chloroform and very slightly soluble in petroleum, hot water, carbon tetrachloride, carbon bisulphide and ether. It was crystallised from alcohol, m. p. 107°. (Found: N, 15·24. $C_{11}H_{12}N_2O$ requires N, 14·89 per cent.).

Cyan-acetbenzylamide.—In the preparation of this substance, Whiteley's method (*J. Chem. Soc.*, 1921, **119**, 370) for the preparation of malon-di-benzylamide was used.

Ethyl cyanacetate (22 g.) and benzylamine (22 g.) were put in a conical flask and refluxed gently on a sand-bath. The substance condensed readily to a yellowish white mass. The heating was stopped after seven hours and the solid was washed with a mixture of benzene and petroleum ether to free it from unchanged reactants. The yield was 90 per cent.

It dissolves readily in benzene, toluene, chloroform, ethyl acetate, acetic acid, methyl alcohol, ethyl alcohol, acetone and nitro-benzene; less readily in carbon bisulphide and hot water, and is sparingly soluble in light petroleum, carbon tetrachloride and ether. It was crystallised from benzene in white long needles, m. p. 120°. (Found: N, 16·19. $C_{10}H_{10}N_2O$ requires N, 16·09 per cent).

Cyanacetmethylamide.—This was prepared by a method corresponding to the method of Whiteley (*loc. cit.*) for the preparation of

malon-di-ethylamide, by shaking a mixture of ethyl cyanacetate
(50 g.) of methylamine (45 g. of 33% solution) and sodium hydroxide
(0·2 g.) for about one hour, at 0°, until it was homogeneous. After
keeping the mixture at the ordinary temperature for twelve hours
the solution was concentrated on a water-bath. On cooling, a reddish
pasty mass was obtained. It was drained on a porous plate when
a mass of granular solid was obtained. The yield was very poor
being about 25 per cent.

It is very soluble in methyl alcohol, ethyl alcohol, chloroform,
ethyl acetate, acetic acid, acetone, water and nitrobenzene; less
soluble in benzene and toluene; and sparingly soluble in carbon
tetrachloride, carbon bisulphide ether and petroleum. It crystallises
in long white needles from benzene, m. p. 101°. (Found: N,
28·85. $C_4H_6N_2O$ requires N, 28·57 per cent.).

Cyanacet-ethylamide.—Ethyl cyanacetate (23 g.) was condensed
with ethylamine (38 g. of 33 per cent solution) in the same way as
cyanacetmethylamide. The yield was about 15 per cent.

It is readily soluble in chloroform, ethyl acetate, acetic acid,
methyl alcohol, ethyl alcohol, water, acetone and nitrobenzene; less
readily in benzene and toluene; and sparingly soluble in carbon tetra-
chloride, carbon bisulphide, ether and light petroleum. It was crystal-
lised from benzene as white needles, m. p. 74°. (Found: N, 25·21.
$C_5H_8N_2O$ requires N, 25·0 per cent.).

CHEMISTRY DEPARTMENT,
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Photobromination of Cinnamic Acid and Stilbene.
Part III.

By Rukmini Mohan Purakayastha and Jnanendra
Chandra Ghosh.

In Part II of this series it was shown that the velocity of this photochemical reaction in green and blue light is given by the equation,

$$k \sqrt{I_0} = \frac{1}{t} \log_e \frac{a}{a-x} + \frac{1}{t} \frac{1}{(c-a)B} \log \frac{a(c-x)}{c(a-x)}$$

where I_0 is the incident intensity, a is the initial concentration of bromine, c is the initial concentration of acceptor molecules and B is a constant given by $Aa^2\tau k\theta$, where a is the distance between the centres of two reacting molecules, τ is the life period of excited molecules, θ the absolute temperature, $k = p/c\theta$ (p is the osmotic pressure in millimeters of mercury, and c the concentration in gram. mol. per litre) and $A = 2666 \cdot 6 \sqrt{\frac{2\pi N}{K} \cdot \frac{m_1 + m_2}{m_1 m_2}}$.

This reaction also takes place in yellow light, but as it is to be expected from the weak absorption of yellow light by the bromine solution, the rate of reaction is given by a modified equation. The concentration of [Br] i.e., active bromine atom is chiefly determined by the reversible reaction, $Br + h\nu \rightleftharpoons 2Br$, and is therefore given by the equation,

$$[Br] = \sqrt{k. I_0 (1 - e^{-\epsilon [Br_2]l})}$$

For weak absorption

$$[Br] = \sqrt{k I_0 \epsilon [Br_2]l} = \sqrt{k' I. [Br_2]}$$

The mechanism of the reaction that has been developed in Part II will therefore give the equation,

$$\frac{dx}{dt} = k \sqrt{I_0} \sqrt{(a-x)} \, (a-x) \, \frac{\tau}{T+\tau} \qquad \ldots \quad (2)$$

$$= k \sqrt{I_0} \, (a-x)^{\frac{3}{2}} \, \frac{B(c-x)}{1+B(c-x)} \qquad \ldots \quad (3)$$

On integration

$$k = \frac{1}{t} \left\{ \frac{1}{(a-x)^{\frac{1}{2}}} - \frac{1}{a^{\frac{1}{2}}} \right\} + \frac{1}{3Bt} \left[\frac{1}{(a-x)^{\frac{3}{2}}} - \frac{1}{a^{\frac{3}{2}}} \right] \ldots \quad (4)$$

If Berthoud's mechanism were correct the velocity constant would have been given by the equation

$$k_1 = \frac{1}{t} \left\{ \frac{1}{(a-x)^{\frac{1}{2}}} - \frac{1}{a^{\frac{1}{2}}} \right\} \qquad \ldots \quad (5)$$

In the following tables are given experimental data which prove definitely that equation (4), and not (5), represents the course of this photochemical reaction.

EXPERIMENTAL.

Experimental procedure is exactly the same as described before.

Yellow light was obtained by using the following filters recommended by Plotnikow.

(1) Potassium permanganate solution—0·375 g. per litre (1 cm. thick).

(2) Potassium chromate solution—150 g. per litre (1 cm. thick).

(3) Nickel sulphate solution—300 g. per litre (2 cm. thick).

Solvent—CS_2; Acceptor—cinnamic acid ;

Initial conc. of cinnamic acid—0·01515 M ;

Initial concn. of bromine—0·01515 M;

Temperature—29°C'; $B = 120$.

TABLE I.

Incident intensity 1305 ergs. per sq. cm. per sec.

Time in min.	$(a-x)$ conc. Br_2 : gm. mol./litre.	k_1 (from Eqn. 5)	k (from Eqn. 4)
0	·01515	...	...
10	·01188	·128	·210
20	·00902	·120	·208
30	·00788	·118	·216
46	·00580	·109	·213
71	·00430	·100	·218

TABLE II.

Incident intensity 810 ergs. per sq. cm. per sec.

0	·01515	...	...
10	·012	·100	·160
20	·0099	·0939	·160
35	·00805	·086	·153
50	·00662	·0807	·158
70	·00534	·0796	·160

TABLE III.

Incident intensity 270 ergs per sq. cm. per sec.

0	·01515	..	...
20	·01213	·0427	·0722
46	·00984	·0425	·0720
69	·0083	·0412	·0724
94	·0070	·0407	·0753 (?)

Solvent CS_2 ; Acceptor—stilbene ;
Initial conc. of bromine—0·01515 M.
Initial conc. of stilbene —0·01515 M.
Temperature 29°C; $B = 360$,

6

TABLE IV,

Intensity 1305 ergs per sq. cm. per sec.

Time in mins,	$(a-x)$ conc. Br_2 : gm. mol./litre.	k_1 (from Eqn. 5)	k (from Eqn.4)
0	·01515	...	...
15	·01105	·0918	·112
30	·0085	·0908	·114
45	·0068	·0898	·115
66	·00528	·0864	·116

TABLE V.

Intensity 810 ergs. per sq. cm. per sec.

0	·01515	...	...
20	·01098	·0713	·0875
40	·0085	·0691	·0852
66	·00635	·0670	·0871

TABLE VI.

Intensity 270 ergs,. per sq. cm. per sec.

0	·01515	...	...
30	·01185	·0855	·0428
60	·00954	·0849	·0433
90	·00803	·099	·0427
132	·0065	·095	·0433

The dependence of the velocity constant on the incident intensity of illumination is given in the following table.

TABLE VII.

Acceptor.	Intensity.	Ratio of velocity constants.	Ratio of intensity.
Cinnamic acid	1305 ergs.	from (1) & (2) 1·35	1·26
	810 ergs.	from (1) & (3) 2·9	2·2
	270 ergs.	from (2) & (3) 2·1	1·73
Stilbene	1305 ergs.	from (1) & (2) 1·31	1·26
	810 ergs.	from (1) & (3) 2·65	2·2
	270 ergs.	from (2) & (3) 2·02	1·73

From the above results it is evident that the velocity constant increases more rapidly than the square root of the incident illumination.

The temperature coefficient of the reaction in yellow light has been measured and found to be 3·1. The results of measurements of the temperature coefficient in blue and green light (Part II) showed that the temperature coefficient increases with the wavelength of incident radiation. The measurements in yellow light also corroborate this.

Induction Period and After-effect.

It had already been noticed that the reaction passes through a period of induction ; the induction period however, in no case is large. It was considered interesting to find out if the reaction is accompanied by an after-effect. It was probable that the active bromine atom or intermediate complex containing bromine would undergo quick transformation in the dark after the illumination is cut off, the reaction ceasing altogether when the active molecular species are completely transformed into stable molecules. It is very difficult to study accurately the velocity of this rapid transformation after cutting off the light. The following tables contain some of the experimental observations. It may be mentioned here that the velocity of reaction in the dark when the period of after-effect is over is very small.

Blue Light.

(Filters as recommended by Plotnikow)

Conc. of bromine—0·01515 M.

Conc. of cinnamic acid—0·01515 M.

Solvent CS_2 ; Temperature 29°C.

TABLE VII.

Time in minutes.	$(a-x)$ conc. Br_2 : gm. mol./litre.	Rate of disappearance of Br_2 in the successive intervals (in one minute).	
0	·01515		
3	·01385		·0006
6	·01125	Exposed to light.	·0007
9	·0099		·00078
12	·0078		·0007

Light cut off.

30	·0067	Darkness	·000061
100	·0062		·0000065

Solvent CS_2 . Initial concentration of bromine—0·01515 M. Initial conc. of stilbene—0·01515 M.

TABLE IX.

Time	$(a-x)$ conc. of Br_2 : gm./mol. litre.	Rate of disappearance of Br_2 in the successive intervals.	
0	·01515		...
3	·01405		·00037
6	·01265	Exposed to light.	·00047
9	·01095		·00057
12	·00930		·00055

Light cut off.

22	·0082	Darkness	·00011
55	·0078		·000012

TABLE X.

Solvent CCl₄. Initial conc. of Br₂—0·01515 M.
Initial of conc. of cinnamic acid —·01515 M.

0	·01515		
5· 5	·0136	Exposed to light.	·00023
11	·0119		·00031
16	·0102		·00034

Light cut off.

45	·0094	Darkness.	.000028
105	·0091		·000005

From the above results it is clear that in the case of these reactions, the induction period is followed by an after-effect when the source of illumination is withdrawn. Another interesting fact has been observed. It appears that if the reacting system is again exposed to light after the induction period and after-effect are over, the reaction passes through another short period of induction. This observation clearly proves that there must be some intermediate complex formation in the process of photobromination. Berthoud's method of varying light intensity by the use of rotating sector is, in this case, open to an obvious objection ; because the successive period of induction and after-effects would certainly prevent the attainment ot equilibrium between the various reacting unstable intermediate molecules which take part in the process of photo-bromination.

ortho-Amino-phenylhydrazine and some Interesting Hetero-cyclic Compounds derived from it. Part III. Lengthened o-Di-derivatives of Benzene and their Ring-closure.

By Prafhulla Chandra Guha and Tejendra Nath Ghosh.

In Part I, Guha and Ray (*J. Indian Chem. Soc.*, 1925, **2**, 86) have shown that 1-*ortho*-nitrophenyl-4-phenylthiosemicarbazide $C_6H_4(NO_2)$. NH.NH.CS. NHPh, on reduction with tin and hydrochloric acid, gives 1-*o*-aminophenyl-4-phenylthiosemicarbazide, which in presence of strong hydrochloric acid loses a molecule of ammonia to yield 2-phenylimino-5:6-benzo-1:2:3:4-tetrahydro-1:3:4-thiodiazine. The present investigation was undertaken with the object of utilising the reactive amino group of several aminophenyl-thiosemicarbazides by condensing with thiocarbimides, carbimides, potassium cyanate, thiocyanate and aldehydes and study the effect of diverse types of ring-closing agents upon the lengthened *ortho*-diderivatives of benzene thus obtained.

o-Nitrophenylhydrazine has now been condensed with tolyl, xylyl and allyl mustard oils to yield three 4-substituted-1-nitrophenylthiosemicarbazides (I, IV, VII). 1-Nitrophenyl-4-tolyl-thio-semicarbazide and 1-nitrophenyl-4-xylyl-thiosemicarbazide on reduction give two compounds in each case, *viz.*, 1-aminophenyl-4-tolyl-thiosemicarbazide (II) and 1-tolyl-2:3-benzo-6-thiol-1:4:5-triazine (III), 1-aminophenyl-4-tolylthiosemicarbazide (V) and 1-xylyl-2:3-benzo-6-thiol-1:4:5-triazine (VI); whereas, from the allyl compound only the corresponding aminophenylthiosemicarbazide (VIII) has been obtained, thus:

$$C_6H_4 \Big\langle \begin{matrix} NH.NH_2 \\ NO_2 \end{matrix} + CH_3C_6H_4.N:C:S$$

$$= C_6H_4 \Big\langle \begin{matrix} NH.NH.CS.NHC_6H_4.CH_3 \\ NO \end{matrix} \quad \xrightarrow{\text{Reduction}}$$

$$\text{(I)}$$

$$C_6H_4 \Big\langle \begin{matrix} NH.NH.CS.NHC_6H_4.CH_3 \\ NH_2 \end{matrix} \quad \text{and} \quad C_6H_4 \Big\langle \begin{matrix} NH{-\!\!-\!\!-}N \\ N{-\!\!-\!\!-}C.SH \\ C_7H_7 \end{matrix} \quad \text{(III)}$$

$$\text{(II)}$$
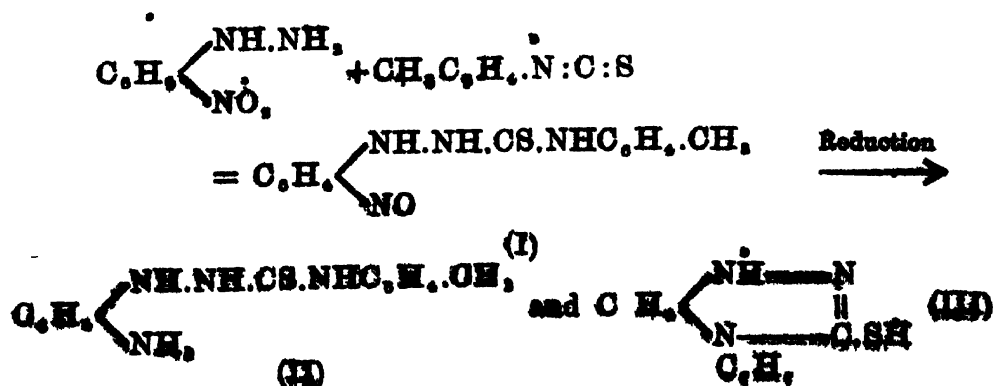
The triazine constitution * of the above ring-closed compounds follows from the fact that they are soluble in cold dilute alkali, give disulphides with iodine, and insoluble mercaptides with mercuric chloride.

1-o-Aminophenyl-4-phenyl, (tolyl, xylyl)-thiosemicarbazide gives the corresponding thiol-triazine compounds when treated with acetic anhydride and strong hydrochloric acid, showing conclusively that during reduction with tin and hydrochloric acid, the nitro group is first reduced to amino which loses ammonia to give rise to the thiol-triazines. Evidently, the ring closure is effected thus :—

$$C_6H_4 \Big\langle \begin{array}{c} NH\text{——}N \\ NH_2 \ NHR \end{array} \Big\rangle C.SH \quad \xrightarrow[\longrightarrow]{-NH_3} \quad C_6H_4 \Big\langle \begin{array}{cc} NH\text{——}N \\ NR\text{——}C.SH \end{array}$$
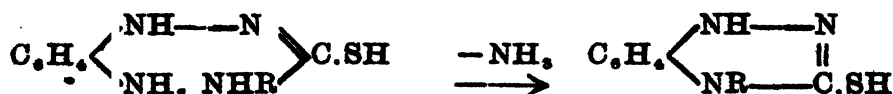
Guha (*J. Amer. Chem. Soc.*, 1923, **45**, 1036) obtained di-*R*-iminothiobiazoles from hydrazinedicarbothioamides by the action of acetic anhydride when H_2S was spilt off (compare also Guha and Guha (*J. Indian Chem. Soc.*, 1927, **4**, 162) who obtained alkylthiol-arylimino-thiobiazoles from thiosemicarbazide-dithiocarboxylates by the elimination of one molecule of sulphuretted hydrogen. It is peculiar that in the present instance ammonia is spilt off instead of sulphuretted hydrogen.

The following lengthened *ortho*-di-derivatives of benzene have been obtained from o-amino-phenyl-4-*R*-thiosemicarbazides by the action of phenyl-, tolyl-, xylyl- and allyl-thiocarbimides.

$$C_6H_4 \Big\langle \begin{array}{c} NH. \ NH.CS.NHPh \\ NH. \ CS.NHPh \end{array} \qquad (IX)$$

$$C_6H_4 \Big\langle \begin{array}{c} NH.NH.CS.NHPh \\ NH.CS.NHC_6H_4.CH_3 \end{array} \qquad (X)$$

$$C_6H_4 \Big\langle \begin{array}{c} NH.NH.CS.NHPh \\ NH.CS.NHC_6H_3(CH_3)_2 \end{array} \qquad (XI)$$

$$C_6H_4 \Big\langle \begin{array}{c} NH.NH.CS.NHPh \\ NH.CS.NHC_3H_5 \end{array} \qquad (XII)$$

$$C_6H_4 \Big\langle \begin{array}{c} NH.NH.CS.NHC_6H_4.CH_3 \\ NH.CS.NHC_6H_4.CH_3 \end{array} \qquad (XIII)$$
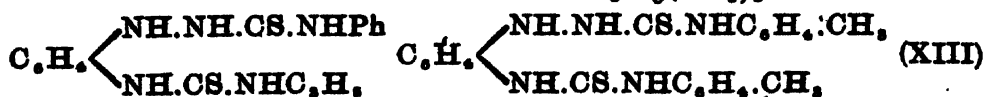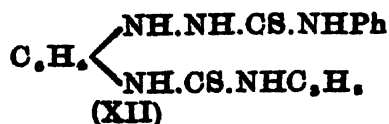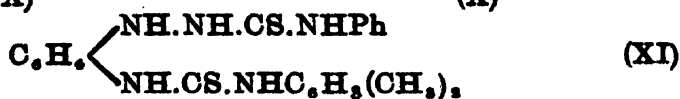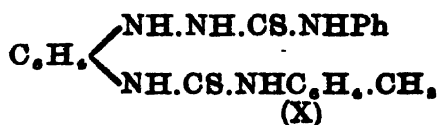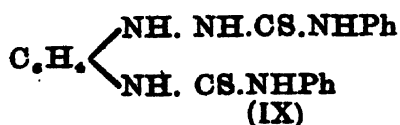
* The benzo-thiodiazine constitution assigned to this compound by Guha and Ray (*loc. cit.*) has now been found to be wrong. It possesses a mercaptanic group due to the presence of which it is soluble in alkali and gives a disulphide. The description of the properties of this substance as given in Part I of this paper is rather inexplicable. It was through some sort of mistake, perhaps, that the properties of some other substance were attributed to this compound.

1-Tolylthiocarbamido-2-phenylthiosemicarbazido-benzene (X) yields on treatment with strong hydrochloric acid 2-tolylamino-4:5-benzo--3-thio-1:2:6:7-octathiotriazine (XIV), thus:—

$$C_6H_4 \begin{cases} NH.NH.CS.NHPh \\ NH.CS.NHC_6H_4.CH_3 \end{cases} \xrightarrow{-C_6H_5.NH_2}$$

$$C_6H_4 \begin{cases} NH—NH—CS \\ N= \end{cases} \quad \begin{matrix} | \\ S \\ | \end{matrix} \quad (XIV)$$
$$NHC_7H_7$$
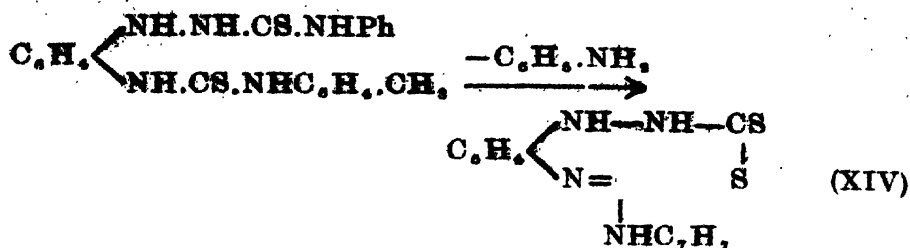
The alternative dimercaptanic formula

$$C_6H_4 \begin{cases} NH—NH—CS \\ NH—\!\!-\!\!-\!\!-CS \end{cases} NC_7H_7$$
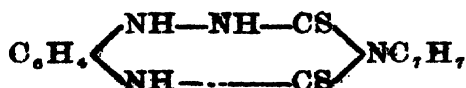
is also possible. By analogy with the formation of amino-thiol-triazole by the ring-closing action of hydrochloric acid upon similar dicarbo-thioamides (Freund and Imgart, *Ber.*, 1895, **28**, 946; Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502) the above constitution has been assigned to the compound (XIV).

1-*o*-Aminophenyl-4-phenylthiosemicarbazide reacts readily with potassium cyanate and phenyl *iso*cyanate to yield 1-carbamido-2-phenylthiosemicarbazido-benzene (XV) and 1-phenylcarbamido-2-phenyl-thiosemicarbazido-benzene (XVI) respectively.

$$C_6H_4(NH_2)NH.NH.CS.NHPh \quad \xrightarrow{KOCN} \quad C_6H_4 \begin{cases} NH.CO.NH_2 \\ NH.NH.CS.NHPh \end{cases} (XV)$$

$$,, \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \quad \xrightarrow{PhNCO} \quad C_6H_4 \begin{cases} NH.CO.NHPh \\ NH.NH.CS.NHPh \end{cases} (XVI)$$
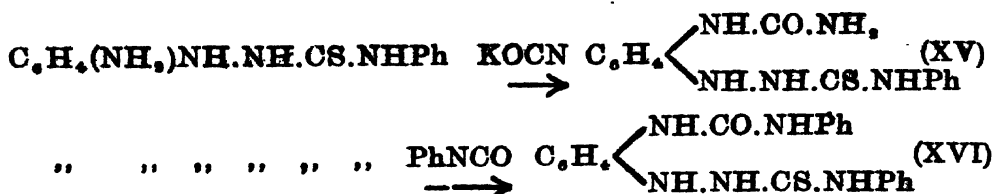
The ring-closure of the above type of lengthened *ortho*-di-derivatives of benzene with strong hydrochloric acid and potassium hydroxide solution gives rise to the identical poly-membered heterocyclic compound, *viz.*, 2:3-benzo-6-phenylamino-9-keto-1:4:5:7-octatetrazine (XVII) thus:—

$$C_6H_4 \begin{cases} NH.CO.NH_2 \\ NH.NH.CS.NHPh \end{cases} \xrightarrow{Conc. \ HCl \ or \ 20\% \ KOH}$$

$$C_6H_4 \begin{cases} NH—CO—NH \\ NH—N=C—NHPh \end{cases} \quad (XVII)$$
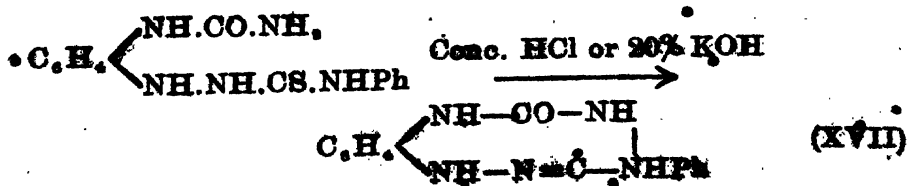
The above compound (XVII) is acidic in character, possibly due to
the presence of the grouping (-CO-NH-) and dissolves in alkali to
form sodium salt. It is worth mentioning that no such ring-
closure of *ortho*-diderivatives of benzene containing the carbonami-
do and thiocarbonamido groupings is known and it is for the first
time that such ring closures have been studied. Freund and Schan-
der (*Ber.*, 1896, **29**, 2506) brought about the ring-closure of the hydra-
zide NH$_2$.CS.NH. NH. CONH$_2$ with hydrochloric acid and obtained
imino-thiobiazolone. The action of caustic alkalis upon this type
of compounds has been found to effect ring-closure not through a
sulphur atom but through nitrogen (Arndt, Milde and Tschenscher,
Ber., 1922, **55**, 341). So it is really interesting to note that it
is immaterial whether the ring-closing agent is an alkali or an acid,
the result in the present instance is the same. The natural
conclusion to be drawn from the above results is that though
different types of ring-closing agents exert their individual influences,
the substances undergoing ring-closure have also got some influence
upon the course of these reactions.

Ferric chloride exerts its oxidising action upon *o*-aminophenyl-4-
R-thiosemicarbazides and forms 3:4-benzo-7-phenylamino-1:2:5:6-
thioheptatriazine (XVIII) and 6:4-benzo-7-tolylamino 1:2:5:6-thio-
heptatriazine (XIX) thus:—
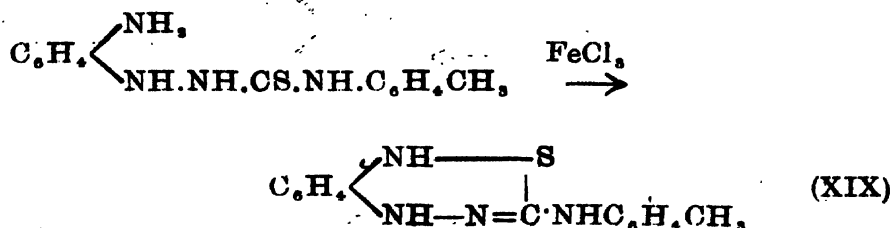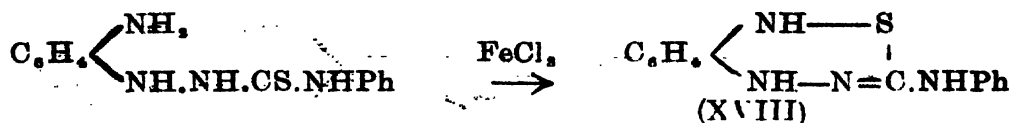
Fromm, Layer and Nerz (*Annalen*, **433**, 1) obtained di-*R*-imino-thio-
biazoles by the action of ferric chloride upon hydrazodithiodicarbona-
mides.

Hydrazine hydrate has also been found to effect the ring-closure
of *o*-aminophenyl-4-*R*-thiosemicarbazides and thus 1-phenyl-3;4-

benzo-7,thiol-1:2:5:6-heptatetrazine (XX) and 1-allyl-8:4-benzo-7-thiol-1:2:5:6-heptatetrazine (XXI) have been obtained thus:—

$$C_6H_4\Big\langle{}^{NH_2}_{NH.NH.CS.NHPh} \longrightarrow C_6H_4\Big\langle{}^{NH_2}_{NH.N:C.SH}\ {}^{NHPh}_{|}$$

$$\longrightarrow C_6H_4\Big\langle{}^{NH\text{------}NPh}_{NH\text{----}N\ =C.SH}\ {}^{NH_2.NH_2}_{|} +2NH_3\ \ (XX)$$
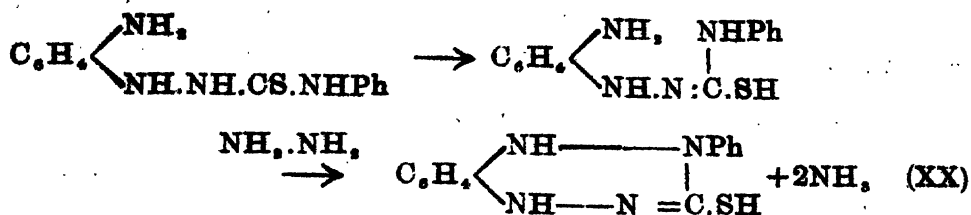
These thiol-benzo-heptatetrazines give all the characteristic reaction of a mercaptan.

Benzaldehyde and *o*-nitro-benzaldehyde have been condensed with *o*-aminophenyl-4-phenylthiosemicarbazide to yield the corresponding benzal (XXII) and *o*-nitrobenzal- (XXIII) derivatives, and the latter on being treated with ferric chloride gives 2-anilino-5:6-benzo-8-nitrophenyl-1:3:4:7-thio-octatriazine (XXIV), thus:—

$$C_6H_4\Big\langle{}^{N:CHPh}_{NH.NH.CS.NHPh}\qquad (XXII)$$

$$C_6H_4\Big\langle{}^{N:CH.C_6H_4NO_2}_{NH.NH.CS.NHPh}\ \xrightarrow{FeCl_3}\ C_6H_4\Big\langle{}^{N:C(C_6H_4NO_2)\text{-}S}_{NH\text{---}N\text{------}C.NHPh}\ {}^{|}$$
$$\qquad\qquad (XXIII)\qquad\qquad\qquad\qquad\qquad (XXIV)$$
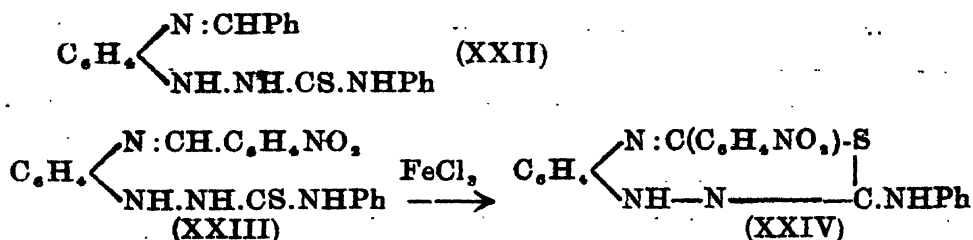
It is quite interesting that though the methenyl hydrogen and the ' thiol hydrogen atoms are so wide apart from each other,. the ring-closure is effected as usual without any hindrance. The formation of these thio-octatriazines bears a very close resemblance. to the process involved in the formation of thiobiazoles from aldehyde-thiosemicarbazones by the oxidising action of ferric chloride as studied by Busch and Holzmann (*Ber.*, 1901, **34**, 324), by Busch and Schneider (*J. pr. Chem.*, 1914, **89**, 314) and by Young and Eyre (*J. Chem. Soc.*, 1901, **79**, 54).

EXPERIMENTAL.

Reduction of 1-o-Nitrophenyl-4-phenylthiosemicarbazide.

The reduction was carried out according to the method of Guha and Ray (*vide* Part 1). By the use of a comparatively less strong hydrochloric acid it has been possible to obtain as much as 3 g.

of 1-o-aminophenyl-4-phenylthiosemicarbazide hydrochloride from 10 g. of the starting material, whereas the older method gave only 1·5 g. The yield of the thiol-benzotriazine has also been raised to 1 g. as against 0·4 g. by the older method.

The free Base, NH$_2$C$_6$H$_4$.NH.NH.CS.NHPh.

The free base was obtained by dissolving the hydrochloride (1 g.) in the least quantity of water and by adding a few drops of sodium carbonate solution to make it just alkaline. A brownish white flocculent mass was thus obtained which was extracted by shaking with ether. The ethereal solution on evaporation yielded a brownish white crystalline mass which was crystallised from alcohol in brownish-white plates, m.p. 102-106° ; yield 0·5 g. (Found : N, 21·58. C$_{13}$H$_{14}$N$_4$S requires N, 21·70 per cent.).

Improved Method of Isolation of Phenyl benzo-thiol-triazine.

The pasty semi-solid mass (compare (ii), *J. Indian Chem. Soc.,* 1925, **2**, 92, 5th line) was suspended in water slightly acidulated with hydrochloric acid and the tarry matter was removed by passing steam through the liquid for two hours. The hot liquid was then further boiled with animal charcoal for half-an-hour and was filtered hot. The solution on cooling and on standing for some time gave beautiful shining white needles, m.p. 151°. It is soluble in hot water, strong hydrochloric acid and cold dilute alkali from the solution of which it can be precipitated by acids.

The Disulphide. — An alcoholic solution of iodine was added drop by drop to an alcoholic solution of the thiol-triazine compound until the solution became reddish-brown in colour. The disulphide was obtained as a yellowish white amorphous powder by the addition of an excess of water to the alcoholic solution. The precipitate was repeatedly washed with a solution of iodine in potassium iodide, with water and finally with alcohol. It was crystallised from methyl alcohol in yellowish white needles, m.p. 175-176°. (Found : S, 13·54. C$_{26}$H$_{20}$N$_6$S$_2$ requires S, 13·88 per cent.).

1-o-*Nitrophenyl-4-p-tolyl-thiosemicarbazide* (I).

An alcoholic solution of o-nitrophenylhydrazine (10 g.) was heated under reflux on the water-bath with p-tolyl-mustard oil (9-10 g.) for about 40 minutes when a yellowish white precipitate was obtained which was crystallised from alcohol, m.p. 176° ; yield

is almost quantitative. It is insoluble in water and acids. (Found: S, 10·91. $C_{14}H_{14}O_2N_2S$ requires S, 10·59 per cent.).

Reduction of Compound (I): *Formation of* 1-o-Aminophenyl-4-p-tolyl-thiosemicarbazide (II) *and* 1-tolyl-2:3-benzo-6-thiol-1:4:5-triazine (III).—The method of procedure was the same as followed in the case of the corresponding phenyl compounds (Part I, *loc. cit.*). The aminophenyl-thiosemicarbazide was purified by adding ether to an alcoholic solution of the substance when it was obtained as a white shining crystalline product, m.p. 252-253° with decomposition and producing a blue colouration. It turns reddish-brown on exposure to the air for some time. (Found: S, 10·67. $C_{14}H_{16}N_4S$ requires S, 10·39 per cent.).

Purification of Compound (III).—It was purified as the corresponding phenyl compound and was finally crystallised from water slightly acidulated with hydrochloric acid in beautiful light yellow rectangular plates, m.p. 182°. It is soluble in cold dilute alkali from which solution it can be precipitated by acids. (Found: N, 16·21. $C_{14}H_{12}N_3S$ requires N, 16·47 per cent.).

The Disulphide of Compound (III) was prepared by the addition of an excess of an iodine solution to an alcoholic solution of the substance and then precipitating it with an excess of water. It melts at 97-98° with decomposition.

Action of Acetic Anhydride upon (II): *Formation of* 1-Tolyl-2:3-benzo-6-thiol-1:4:5-triazine (III).—1-o-Aminophenyl-4-p-tolylthiosemicarbazide hydrochloride (1 g.) was heated with acetic anhydride (4 c.c.) on a sand-bath under reflux till a clear brownish coloured solution was obtained. The reaction mixture was then poured into cold water and thus a slight yellow precipitate was obtained and a second crop was obtained by concentrating the mother-liquor. The product was then crystallised from water slightly-acidulated with hydrochloric acid, in light yellow needles melting at 182°. (Found: N, 16·23. $C_{14}H_{12}N_3S$ requires N, 16·47 per cent.). The identity of this compound with (III) was proved by taking the mixed melting point.

1-o-*Nitrophenyl*-4-(1:3:4)-*xylyl-thiosemicarbazide* (IV).—An alcoholic solution of o-nitrophenyl hydrazine (10 g.) and xylyl-mustard oil (11 g.) was heated on a water-bath under reflux for about an hour when a yellow crystalline product came out of the solution. The product was further crystallised from alcohol, m.p. 112°; yield

about 19 g. (Found: S, 10·51. $C_{18}H_{18}O_2N_6S$ requires S, 10·12 per cent.).

Reduction of the above Compound: Formation of 1-o-Amino-phenyl-4(1:3:4)-xylyl-thiosemicarbazide (V) *and 1-Xylyl-2:3-benzo-6-thiol-1:4:5-triazine* (VI).—The reduction was carried out by following the methods as adopted in the case of the phenyl and tolyl compounds. The thiosemicarbazide (V) was purified by adding ether to an alcoholic solution of the substance when a white shining crystalline mass was obtained which melted at 255-256° with decomposition and producing a blue colouration. It turns reddish-brown on standing. (Found: S, 10·27. $C_{15}H_{18}N_4S$, HCl requires S, 9·94 per cent.).

The benzo-triazine compound was purified similarly as the corresponding phenyl compound and was crystallised from water slightly acidified with hydrochloric acid in shining white plates, m.p. 173-174°. (Found: N, 15·43. $C_{16}H_{15}N_3S$ requires N, 15·61 per cent.).

Action of Acetic Anhydride upon Compound (V): *Formation of 1-Xylyl-2:3-benzo-6-thiol-1:4:5-triazine* (VI).—The usual method of preparation was adopted in this case and the resulting product was crystallised from dilute hydrochloric acid in white shining plates, m.p. 173-174°. (Found: N, 15·45. $C_{16}H$ N_3S requires N, 15·61 per cent.).

1 o-Nitrophenyl-4-allyl-thiosemicarbazide (VII).—An alcoholic solution of o-nitrophenylhydrazine (10 g.) and allyl mustard oil (7 g.) was heated under reflux on a water-bath for two hours. On pouring the reaction mixture to cold water (200 c.c.) a yellow crystalline product separated out which was further purified by crystallisation from alcohol, m.p. 160°. It is insoluble in water and acids but readily soluble in alkali producing a beautiful bluish violet colouration. (Found: N, 22·42. $C_{10}H_{12}O_2N_4S$ requires N, 22·22 per cent.).

Reduction of Compound (VII): *Formation of 1-o-Aminophenyl-4-allyl-thiosemicarbazide* (VIII).—1-o-Nitrophenyl-4-allyl-thiosemi-carbazide (10 g.), granulated tin (10 g.) and concentrated hydrochloric acid (60 c.c.) were heated on a water-bath for three to four hours. The contents of the flask were then largely diluted with water and tin removed by passing sulphuretted hydrogen repeatedly. The solution was evaporated almost to dryness on the water-bath which on cooling yielded a brownish red crystalline mass. The raw product

thus obtained was purified by adding ether to an alcoholic solution of the substance when white shining crystals, m.p. 247-248° with decomposition were obtained. It turns reddish-brown on standing for some time. (Found: S, 12·15. $C_{10}H_{14}N_4S$, HCl requires S, 12·40 per cent.).

1-*Phenylthiocarbamido*-2-*phenylthiosemicarbazido-benzene* (IX).— An alcoholic solution of 1-*o*-aminophenyl-4-phenylthiosemicarbazide (2 g.) and phenyl mustard oil (1 g.) was heated on the water-bath under reflux for three hours. The reaction product on being poured into water gave a white solid which was crystallised from dilute alcohol in shining white rectangular plates, m.p. above 290°. It is soluble in hot water and in cold concentrated alkali; yield 2 gms. (Found: S, 16·48. $C_{20}H_{19}N_5S_2$ requires S, 16·29 per cent.).

1-p-*Tolylthiocarbamido*-2-*phenylthiosemicarbazido-benzene* (X).— The method of preparation was the same as in the case of the preceding compound (IX). From 2 g. of 1-aminophenyl-4-phenyl-thiosemicarbazide hydrochloride and 1 g. of *p*-tolyl-mustard oil about 2 gms. of the product were obtained. It was crystallised from dilute alcohol in shining white plates which did not melt even at 290°. (Found: S, 15·28. $C_{21}H_{21}N_5S_2$ requires S, 15·72 per cent.).

1-*Xylylthiocarbamido*-2-*phenylthiosemicarbazido-benzene* (XI).— The method of preparation was the same as in the case of the two preceding compounds. The yield of the product was 1·2 g. from 1-*o*-aminophenyl-4-phenylthiosemicarbazide hydrochloride and xylyl mustard oil (0·7 g.). It was crystallised from alcohol in white shining plates which did not melt even at 290°. (Found: S, 15·88. $C_{22}H_{23}N_5S_2$ requires S, 15·20 per cent.).

1-*Allylthiocarbamido*-2-*phenylthiosemicarbazido-benzene* (XII).— The method of preparation was the same as the preceding compound. It was crystallised from dilute alcohol in white shining plates which did not melt even at 290°; yield 1·g. (Found: S, 18·28. $C_{17}H_{17}N_5S_2$ requires S, 17·92 per cent.).

1-p-*Tolylthiocarbamido*-2-p-*tolylthiosemicarbazido-benzene* (XIII). —The reaction product was crystallised from dilute alcohol in white shining plates, m.p. 281-282°. (Found: S, 15·55. $C_{22}H_{23}N_5S_2$ requires S, 15·21 per cent.).

Action of strong Hydrochloric Acid upon 1-p-*Tolyl-thiocarbamido-* 2-*phenylthiosemicarbazido-benzene: Formation of* 2-*Tolylamino-* 4:5 *benzo-8-thio-1:3:6:7-octathiotriazine* (XIV).—1-p-Tolylthiocarba-

mido-2 phenylthiosemicarbazido-benzene (1 g.) was heated under
reflux with concentrated hydrochloric acid (d 1·19). After
about 20 minutes' heating the substance went into solution and on
continuing the heating for another 20 minutes, white shining crys-
tals began to come out of the solution. The solution was allowed to
cool, filtered, precipitate washed with water and was finally crystal-
lised from alcohol, m.p. 200°. It is insoluble in water but it readily
dissolves in cold dilute alkali. The presence of aniline in the acid
filtrate was tested by diazo reaction and coupling with β-naphthol.
(Found: N, 17·52. $C_{14}H_{14}N_4S_2$ requires N, 17·88 per cent.).

1-*Carbamido-2-phenylthiosemicarbazido-benzene* (XV).—Potassi-
um cyanate (0·3 g.) dissolved in the minimum quantity of water was
added slowly to 1-o-aminophenyl-4-phenylthiosemicarbazide hydro-
chloride (1 g.) also dissolved in the smallest quantity of water under
cooling. The reaction took place at once and a white solid mass
came out which was filtered, washed with water and finally crystal-
lised from dilute alcohol in brownish white plates. It did not melt
even at 290°; yield 0·8 gm. (Found: N, 23·02. $C_{14}H_{13}ON_5S$
requires N, 23·25 per cent.).

Action of Hydrochloric Acid upon (XV): *Formation of 2:3-Benzo-
6-phenylamino-8-keto-1:4:5:7-octatetrazine* (XVII).—Two gms.
of the compound (XV) were heated with strong hydrochloric acid
(50 c.c.) under reflux for about an hour and the reaction product was
poured into water when a brownish white crystalline mass came
out. It was filtered, washed with water and crystallised from alco-
hol in brownish white shining plates, m.p. 145°; yield 1·3 g.
(Found: N, 25·99. $C_{14}H_{13}ON_5$ requires N, 26·21 per cent.).

Treatment of Compound (XV) *with 20% Potassium Hydroxide
Solution: Formation of Compound* (XVII).—Two g. of the compound
(XV) were heated with about 40 c.c. of the potassium hydroxide
solution for an hour and a half. The clear solution thus obtained
was neutralised with dilute hydrochloric acid under cooling when
sulphuretted hydrogen was profusely evolved with the separation of
a brownish white crystalline mass which was twice crystallised from
dilute alcohol, m.p. 145°. (Found: N, 25·84. $C_{14}H_{13}ON_5$ requires
N, 26·21 per cent.). The identity of this compound with the pre-
ceding one was confirmed also by taking a mixed melting point.

1-*Phenylcarbamido-2-phenylthiosemicarbazido-benzene* (XVI).—
Phenylisocyanate (0·6 g.) was slowly added under cooling to 1-o-

aminophenyl-4-phenylthiosemicarbazide hydrochloride (2 g.) dissolved in water and the mixture was shaken vigorously for about ten minutes. The reaction took place with the evolution of heat and a brownish flocculent mass separated out which was crystallised from dilute alcohol, m.p. above 290°. (Found: N. 18·82. $C_{20}H_{16}ON_5$ S requires N, 18·56 per cent.).

Action of Ferric Chloride upon 1-Aminophenyl-4-phenylthiosemi carbaside: *Formation of 3:4-Benzo-7-phenylamino-1:2:5:6-thioheptatriazine* (XVIII).—Excess of ferric chloride solution was added to 1-*o*-aminophenyl-4-phenylthiosemicarbazide hydrochloride (2 g.) when the solution turned reddish brown; the solution was then heated to boiling for about an hour and filtered hot. The crystalline product thus obtained was crystallised from water slightly acidulated with hydrochloric acid as red needles, m.p. 140°. It was the hydrochloride of a base as was proved by the fact that it gave silver chloride with silver nitrate solution. It is excessively soluble in cold water. (Found: N, 19·21; Cl, 11·54. $C_{19}H_{12}N_4S$, HCl requires N, 19·17; Cl, 11·98 per cent.).

3:4-Benzo-7-p-tolylamino-1:2:5:6-thioheptatriazine (XIX).—The method of preparation was the same as in the case of the compound (XVIII). It was crystallised from water slightly acidulated with hydrochloric acid in beautiful reddish brown needles which did not melt even at 290°. It is very soluble in water and gives silver chloride with silver nitrate solution. (Found: N, 18·23; Cl, 11·21. $C_{14}H_{12}N_4S$, HCl requires N, 18·30; Cl, 11·43 per cent.).

Action of Hydrazine Hydrate: Formation of 1-Phenyl-3:4-benzo-7-thiol-1:2:5:6-heptatriazine (XX).—An alcoholic solution of 1-*o*-aminophenyl-4-phenylthiosemicarbazide (2 g.) and hydrazine hydrate (0·4 g.) was heated under reflux for about an hour. The solution on cooling gave a brownish white crystalline mass which was filtered, washed with alcohol and then with water and was crystallised from alcohol as white shining plates, m.p. 83-84°. It is soluble in hot water- and in cold dilute alkali and gives an amorphous yellow disulphide with iodine solution and a yellowish white mercaptide with mercuric chloride. (Found: N, 22·09. $C_{13}H_{12}N_4S$ requires N, 21·87 per cent.).

1-Allyl-3:4-benzo-7-thiol-1:2:5:6-heptatetrazine (XXI).—The method of preparation was the same as that of the preceding compound (XX). The reaction product was crystallised from alcohol,

m.p. 81-82°. It was soluble in hot water and in cold dilute alkali. It gave an amorphous disulphide with iodine solution and a yellowish white mercaptide with mercuric chloride. (Found: N, 15·29. $C_{1_2}H_{1_2}N_4S$ requires N, 25·45 per cent.).

1-*Benzalanilino*-4-*phenylthiosemicarbazide* (XXII).

A dilute alcoholic solution of 1-o-aminophenyl-4-phenylthiosemi-carbazide (2 g.) and benzaldehyde (0·7 g.) was heated on a water-bath under reflux for two hours. Some alcohol was then distilled off and the residual solution on dilution with water gave a white solid mass. Any unconverted benzaldehyde was removed with steam and the solution was filtered hot which on cooling yielded a white crystalline mass which was crystallised from boiling water in white needles, m.p. 168-169°; yield 1·5 g. (Found: N, 16·33. $C_{2_0}H_{1_8}N_4S$ requires N, 16·18 per cent.).

1-o-*Nitrobenzalanilido*-4-*phenylthiosemicarbazide* (XXIII).—A dilute alcoholic solution of 1-o-aminophenyl-4-phenylthiosemicarba-zide (2 g.) and o-nitrobenzaldehyde (1 g.) was heated on a water-bath under reflux for 2-3 hours. On cooling greyish white crystals gradually came out of the solution which were filtered, washed with alcohol and crystallised from a mixture of alcohol and acetic acid as brownish white needles, m.p. 260°. It is sparingly soluble in hot water, readily soluble in acetic acid, acetone and alcohol; yield 1·5 g. (Found: N, 17·79. $C_{2_0}H_{1_7}O_2N_5S$ requires N, 17·9 per cent.).

Action of Ferric Chloride upon (XXIII): *Formation of 2-Anilino-5:6-benzo-8-nitrophenyl-1:3:4:7-thio-octatriazine* (XXIV).—1-Nitro-benzalanilido-4-phenylthiosemicarbazide (1 g.) was heated with an excess of ferric chloride solution (2 g. dissolved in 13 c.c. of dilute hydrochloric acid) for about an hour and the solution was filtered hot. On cooling, the filtrate gave beautiful shining brownish col-oured crystals' which were filtered, washed repeatedly with water and was crystallised from dilute hydrochloric acid, m.p. 216-217°. It gave silver chloride with silver nitrate solution. (Found: N, 16·88. $C_{2_0}H_{1_5}O_2N_5S$, HCl requires N, 16·47 per cent.).

Our thanks are due to Sir P. C. Ray and Prof. J. C. Ghosh for the kind interest they have taken in this work.

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Page	Line	
51	13 (Formula II)	Read $O = \overset{1}{C} - \overset{1}{C} = \overset{H}{C} \cdot OH$
322	4	For "90g." read "9·0g."
475	15	Read "$2(C_6H_5)_2NH$"
431	15	For "only 6g." read "only 0·6g".
432	15	For "manganese dioxide" read "manganese hydroxide"
435	10	For "rare earth" read "rare earth oxide"
,,	*9	For "2 small pieces" read "small pieces"
436	19	For "rose from" read "rose slowly from"
468	2	For "$PtCl_{11}$ $2Et_2s$" read "$PtCl_3$, $2Et_2S$"
,,	*9	For "$PtCl_3$ $3C_2H_4(NH_2)_2$" read "$2PtCl_3$, $3C_2H_4(NH_3)_2$"
,,	*3	For "AgCl NH" read "AgCl NH_3"
340	*6	For "$C_{10}H_{12}NO$" read "$C_{10}H_{12}N_2O$"
342	17	For "90-32°" read "90-92°"
402	20	For "4-Acetylamino-2-phenyl stibinate of sodium" read "4-Acetylamino-3-bromophenyl stibinate of sodium".

* From bottom.